RUBBER CHEMISTRY AND TECHNOLOGY

VOLUME XI NUMBER 3

July, 1938

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RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the Editor representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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Cancellation of Meeting of The Rubber Division at Milwaukee, September, 1938

The Executive Committee hereby notifies the membership of The Rubber Division that the divisional meeting scheduled to be held during the Fall Meeting of The American Chemical Society in Milwaukee has been cancelled. This action has been taken because only three papers were submitted for presentation.

It is hoped that the cancellation of this meeting because of lack of papers will stimulate the membership of The Rubber Division to greater activity in the preparation of manuscripts. The officers request that all members anticipate the Baltimore meeting by giving serious consideration now to the planning of material which may be presented there.

The election of officers for 1939 will be conducted in September by mailed ballots.

H. I. CRAMER, *Secretary*

The American Society of Mechanical Engineers Committee on Rubber and Plastics

The following announcement concerning the organization of a Committee on Rubber and Plastics by the American Society of Mechanical Engineers has been received:

"That applications of rubber and plastics are rapidly forging ahead is clearly evident from the attention now being devoted to these materials. Indicative of the trend, the American Society of Mechanical Engineers recently established a committee, or subdivision, on rubber and plastics, which will deal with several phases of the rubber and plastics industries including mechanical applications, research on basic mechanical properties, processing equipment and standards. Activities of the group will be beyond the normal range of other professional organizations in an effort to fill the present conspicuous gap in the mechanical field.

"The committee will sponsor the presentation of papers at technical sessions of the regular quarterly meetings of the A. S. M. E. A symposium on rubber, comprising four invited papers covering the history of rubber, synthetic substances with rubber-like properties, fabrication of rubber parts, and certain mechanical properties of rubber, is included in the program of the next meeting of the society to be held at Providence, October 5–7. Participation in activities of the committee will not be restricted to members of the parent society.

"Authors of papers believed suitable for presentation at subsequent quarterly meetings should communicate at least four months in advance with Dr. J. F. Smith, Edward G. Budd Mfg. Company, 25th Street and Hunting Park Avenue, Philadelphia, Pennsylvania, Secretary of the Rubber and Plastics Committee; or with the Chairman, Dr. F. L. Yerzley, E. I. du Pont de Nemours & Co., P. O. Box 525, Wilmington, Delaware."

New Books and Other Publications

Annual Report on the Progress of Rubber Technology. Vol. 1—1937. Published by the Institution of the Rubber Industry, 12, Whitehall, London, S. W. 1, England. $7^1/_4 \times 9^3/_4$ in. 160 pp. Price to members: 5s (approximately $1.25); non-members: 10s 6d (approximately $2.60).

Several years ago the Council of the Institution of the Rubber Industry first gave consideration to the publication of a series of systematic annual reports on the progress of world-wide rubber technology. The result is found in the current report covering the year of 1937, the first of what is expected to be a series of annual reports. It will be recalled that somewhat corresponding reports covering the American rubber industry appeared in the "Annual Survey of American Chemistry," published each year from 1925 to 1935 by the National Research Council. An effort to continue this work was made by the Carnegie Institute of Pittsburgh, but the only volume to appear was the "Annual Survey of American Rubber Chemistry for 1936." The British work, however, is more complete and is world-wide in scope.

The object of the reports is to epitomize the principal steps of advancement in all branches of the rubber industry. To attain this end, the Council invited a number of experts distinguished in special branches of the industry to prepare a survey of progress made in their particular section. The surveys, edited by T. J. Drakeley, are presented in this first report. The breadth of the undertaking may best be realized from the subject heads, a list of which follows:

History, General and Miscellaneous, and Statistics (J. P. Griffiths); Planting and Production of Raw Rubber and Latex, Including Gutta-Percha, Balata, Chicle and Jelutong, the Applications of These Products (B. J. Eaton); The Properties, Applications and Utilization of Latex, Including Treatment of Fabric with Latex (F. H. Cotton); Chemistry and Physics of Raw Rubber, Gutta-Percha, Chicle, Balata, Jelutong (C. A. Redfarn and P. Schidrowitz); Synthetic Rubber (W. J. S. Naunton); Testing Equipment, General, and Specifications other than Latex (Geo. Martin); Compounding Ingredients, General Vulcanizing Accelerators, Antioxidants and Softeners (W. J. S. Naunton); Fabrics and Textiles (W. Knight); The Chemical and Physical Properties of Vulcanized Rubber (R. W. West).

Tires (J. G. Mackay); Belting (H. Rogers); Hose and Tubing (H. Rogers); Cables and Electrical Insulation (C. J. Beaver); Footwear (A. Johnston); Games, Sports Accessories, Toys (J. G. Mackay); Mechanical Rubber Goods (H. Rogers); Roads (G. E. Coombs); Rubber Flooring (H. Rogers); Surgical Goods (C. R. Punnell); Textile-Rubber Composites, Solvents, Cements (W. N. Lister); Sponge Rubber (J. D. Campbell); Hard Rubber (H. A. Daynes); Works Processes, Materials, Including the Treatment of Raw Rubber in the Factory, and the Treatment of Vulcanized Rubber (S. S. Pickles); Machinery and Appliances (Colin Macbeth).

It is evident from the above titles and the names of authors that no effort has been spared to cover all branches of the rubber industry and that the most eminent British rubber technologists were called upon for contributions to the survey. The Research Association of British Rubber Manufacturers aided materially in the preparation of the report. W. J. S. Naunton formulated the plan upon which the Council resolved to issue the annual reports. The first edition, which is complete with author and subject indexes, and which gives extensive references at the end of each subject, is highly commendable, and it is to be hoped that there will be no break in the publication of the reports. [From *The Rubber Age* of New York.]

Rubber Producing Companies—1938. Compiled by the Mincing Lane Tea & Rubber Share Brokers' Association, Ltd., Plantation House, Mincing Lane, London, E. C. 3, England. Published by *The Financial Times*, 72 Coleman St., London, E. C. 2. Boards, 605 pp. $5^1/_4 \times 8$ in. Indexed. Price, 7s 6d.

Following the lines of previous editions, this annual reference work contains information, chiefly financial, concerning approximately 600 companies producing crude rubber. The data shown include: date of registration, list of directors and secretaries, financial structure, acreage, crops, profit and dividends, and other relevant information. Each company is described separately in alphabetical order throughout the book.

The preface points out that, although the amount of rubber wanted for use will be probably less in 1938 than in 1937, there lies a strong foundation of confidence for future demand, a confidence based on the fact that rubber is essential in a world where mechanization, speedy transport, and electrification are ever increasing and becoming more universal. [From the *India Rubber World.*]

Kautschuk: Wandlungen in der Erzeugung und der Verwendung des Kautschuks nach dem Weltkrieg. Heinz George. Published by Bibliographisches Institut A. G., Leipzig, Germany. Paper, 210 pp. $6^1/_4 \times 9$ in.

Changes in production and use of rubber after the World War form the subject of this book, which is number nine in the series "Wandlungen in der Weltwirtschaft" (Changes in World Economics), edited by Hermann Schumacher. Clearly, impartially, and without going into too great detail, George presents his graphic survey which he divides into four parts: Changes in Rubber Consumption, Changes in Rubber Production, Market Problems, and Attempts at Market Regulation.

In the first section the part played by the United States as consumer of rubber and the developments of American consumption for tires and other rubber goods receive special attention. The most important developments in the production of crude rubber, the financial set-up of estates with itemized cost of production, and latest estate methods, as well as recent work in synthetic rubber, are next covered. The problems of stocks and price fluctuations are then briefly but clearly discussed. The final section discusses the Stevenson Restriction Scheme, its effects on non-British planting in the Far East, American experiments in planting rubber in Africa and South America, the lessons taught by the mistakes in connection with this scheme, and lastly, the slump after 1929 and the present rubber regulation scheme.

Numerous tables have been introduced in the body of the book, and in addition a statistical appendix is provided giving data for world net imports of crude rubber, areas under plantation rubber, exports of crude rubber, highest and lowest London prices, etc. There is also a fairly extensive bibliography.

Professor Schumacher in his foreword acknowledges the assistance of the Rockefeller Foundation and the work of F. M. Judd, of New York. [From the *India Rubber World.*]

Schedule of Rubber Goods Manufactured by Società Italiana Pirelli. Società Italiana Pirelli, Milan, Italy. $6^3/_4 \times 9^1/_2$ in. 32 pp. (In English.)

The wide range of rubber products made by Pirelli are alphabetically listed under various classifications in this catalog. The classifications include surgical, sanitary, and toilet articles; mechanical goods; sponge rubber products; sporting goods and games; household items, clothing; stationery products; and miscellaneous. [From *The Rubber Age* of New York.]

Symposium on Consistency. American Society for Testing Materials, 260 South Broad St., Philadelphia, Penna. 6 × 9 in. 74 pp. 85¢.

In addition to a review of present-day practices, this symposium includes a discussion of theoretical background and existing nomenclature, and also considers the possibilities of standardization in consistency measurements. Nine technical papers with considerable discussion comprise the publication. Materials discussed include rubber and rubber compounds, coal tar, petroleum products, asphalts, plastics, and insulating materials. The Symposium was originally held in New York City in June, 1937. [From *The Rubber Age* of New York.]

The Use of Rubber in Furniture. Rubber Growers' Association, Inc., 19 Fenchurch St., London, E. C. 3, England. 6 × 9 in. 24 pp.

As the title indicates, this booklet covers the use of rubber in furniture, including seatings, stuffing materials, and upholstery fabrics. The history of such use is also covered. Several illustrations are included The booklet is a reprint of an article which appeared in the September, 1937, issue of the *R. G. A. Bulletin.* [From *The Rubber Age* of New York.]

Report on Pneumatic Tyred Carts and Other Equipment. British Rubber Publicity Association, 19 Fenchurch St., London, E. C. 3, England. 6 × 9½ in. 16 pp.

The British Rubber Publicity Association has taken over the activities hitherto carried out by the Rubber Growers' Association in connection with propaganda and publicity for rubber products and the development of new uses for rubber. This is the first report under the new arrangement. As indicated by the title, it describes and illustrates various types of rubber-tired agricultural equipment (as used on the University of Reading Farm, at Sonning-on-Thames, in England). The larger portion of the report is devoted to an article on "A Comparison of the Draw Bar Pull of Farm Carts Running on Pneumatic Tyres and Iron Tyres," by J. B. Passmore and M. H. R. Soper. [From *The Rubber Age* of New York.]

Technical Books of All Publishers. Catalog No. 6. Chemical Publishing Co., 148 Lafayette St., New York, N. Y.

This 145-page catalog lists and describes chemical, bacteriological, pharmaceutical, medical, engineering, electrical, and general scientific and other technical books of all American and British publishers. Copies will be sent upon the receipt of 10¢ in stamps or coin to cover mailing costs. [From the *India Rubber World.*]

[Reprinted from the Journal of the Rubber Research Institute of Malaya, Vol. 8, No. 2, pages 179–196, January, 1938.]

The Components of Hevea Latex

Part II. Seasonal Variations in the Composition of Typical Seedling Latex

K. C. Roberts

Rubber Research Institute of Malaya, Kuala Lumpur

Introduction

The problem of the variability of latex and of plantation rubber has hitherto been approached mainly from the point of view of field and factory practice. Absence of standardized procedure and of clean technic in the handling of latex and the manufacture of raw rubber clearly tends to the production of a non-uniform product. But despite all advances in this direction, consumers continue to report considerable variations in the physical properties of latex ammoniated for export and of raw rubber, and in the behavior of the latter on vulcanization.

It is now apparent that considerable variation is inherent in latex itself, presumably determined by such factors as climate, genetic strain of the tree, type of soil, and topography. Attention is therefore now being directed towards tracing, by analytical means, variations in the composition of latex (and therefore of raw rubber) which have their origin in such factors. The work of Wiltshire (Rubber Res. Inst. Malaya, *Bull.* No. 5) in this field covered a 12-month period, and dealt with variations in the dry-rubber content and the inorganic components of latex.

Scope of Present Work

The present paper describes the results of observations covering a similar period, June, 1936–May, 1937, inclusive, and deals with the variations, qualitative and quantitative, of all known naturally occurring components of latex. The method of analysis has been that described in Part I of this series (cf. Roberts, *J. Rubber Res. Inst. Malaya*, **7**, 46 (1936); Rubber Chem. and Tech., **10**, 1 (1937)), and the observations therefore deal with the ammonium salt, the ester, the fatty acid complex, the phosphate complex,* crude caoutchol,* and the rubber hydrocarbon itself. Throughout the period, fresh latex from an estate in the neighborhood of the Institute has been subjected to analysis as frequently as circumstances permitted, *i. e.*, on an average of 5–6 times per month. At the same time records have been kept of rainfall, incidence of wintering, region of estate from which the latex was drawn, and variations in tapping practice. The effect of the last-mentioned controllable factor on the composition of latex will be discussed in a later communication.

Results

Ammonium Salt.—This component was obtained during the 12-month period in forms ranging from a colorless crystalline solid (cf. Plate IA) to a brown gummy

* The components now named "phosphate complex" and "crude caoutchol" correspond to the "protein complex" and the "sulfur complex" of Part I. These changes have become necessary in the light of further knowledge of the nature of these components. Nitrogenous matter is less characteristic of the "protein complex" than its phosphate material, while the most characteristic feature of the former "sulfur complex" is not so much its sulfur content, as a new alcoholic component, which has been named caoutchol. A detailed account of this will appear in the near future.

material. It varied widely in amount (cf. Table I), but the amount was at most only small. For this reason, and also because it is frequently associated with a considerable proportion of quebrachitol, no particular significance may be attached to this variation. Variations in both quality and quantity were frequent and irregular, and no correlation has been established between them and any other factor. It may however be remarked that the amounts isolated tended to be low for several months (June–December, inclusive), during which the rainfall was below the average for that period (cf. heavy black line, Graph II).

It is believed that this material consists essentially of a relatively simple substance which is rapidly used and renewed by the tree in the synthesis of more complex substances.

Ester.—This component, the ligroin-insoluble portion of the acetone-soluble substances, was observed at various times as a red oil, a wax-like solid, and a coarsely crystalline mass. The last-mentioned occurrence was due to the inclusion of a considerable proportion of quebrachitol. Quantitative variations closely followed those of the "ammonium salt" (cf. Table I).

TABLE I

Constituent	Per Cent of Latex Total Solids			
	Lowest Value	Highest Value	Mean	No. of Specimens
Ammonium salt	0.01	0.23	0.06	55
Ester	0.04	0.26	0.12	49
Fatty acid complex	1.11	2.46	1.58	64
Crude caoutchol	1.25	4.66	2.39	62
Phosphate complex	3.54	6.23	4.90	42
Crude hydrocarbon	84.70	93.70	88.97	39

Fatty Acid Complex.—Qualitatively, this component showed but little variation throughout the period of observation. It ranged from a deep yellow to a dark red oil, which in all cases deposited crystals when kept, (Plate IB), though with varying degrees of facility. The quantitative range is shown in Table I. Since the complex is a component of a biological fluid, a considerable variation such as that observed is not surprising. In view of the familiar use of the fatty acids as softeners of rubber, the observed variation is almost certainly large enough to be significant from the point of view of variability in the physical properties of raw rubber.

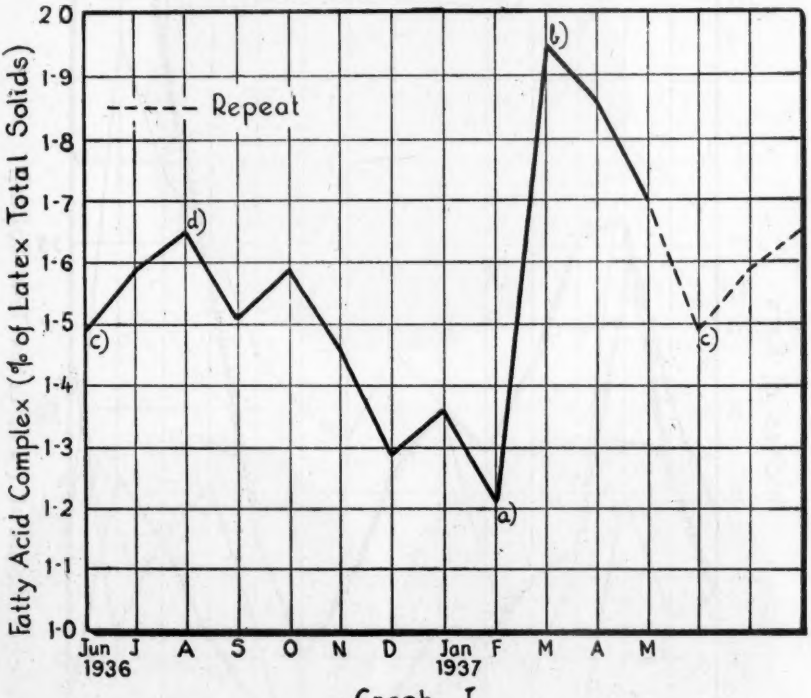
The factor chiefly responsible for quantitative variations in the fatty acid complex appears to be the incidence of wintering. Reference to Graph I shows a pronounced minimum value (*a*) for February, when wintering was in progress. This point is followed immediately by an equally pronounced maximum (*b*) in March, and a further high value for April, these two months corresponding to the period of maximum refoliation activity. Thereafter the curve drops to a secondary minimum in June (*c*) which precedes a rise to a secondary maximum (*d*). It is perhaps significant that these subsidiary features coincide with the period of seed development in the tree (June to August). Other irregularities in the curve are too small to be significant.

Crude Caoutchol.—This component varied widely in texture from specimen to specimen. During the period under review specimens were observed ranging from a dark brown, tacky, semi-fluid mass to a light brown, non-tacky elastic solid. The variation in amount recorded in Table I (1.25 to 4.66 per cent of latex total solids) is notable, and can scarcely fail to be of critical importance in determining the properties of latex and rubber. This is particularly the case since it has been found that the rubber hydrocarbon purified by removal of caoutchol is almost devoid of elasticity. The plasticity and vulcanization tests necessary to establish a

correlation between caoutchol content and the properties of rubber will be undertaken in this laboratory in the near future.

Although no final conclusion has yet been drawn as to the causes of the variation in nature and amount of caoutchol, there does seem to be a connection between the amount of caoutchol and rainfall. This is revealed by a comparison of the monthly average values of the amounts of the component with the rainfall statistics, as shown in Graph II.

The periods of high rainfall (March–May, 1936; January–April, 1937) are seen to be accompanied by a rising tendency in the curve representing monthly average amounts of caoutchol (jagged line), while the period June–December, 1936, during

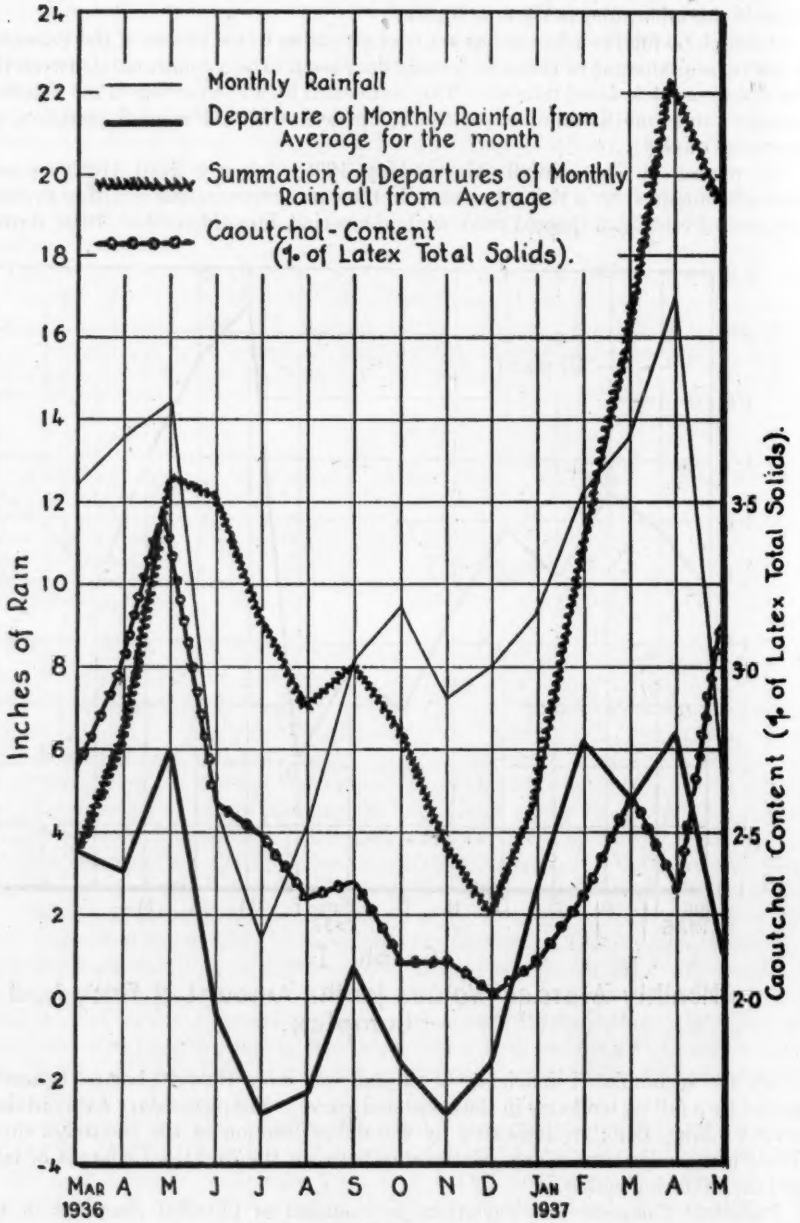


Graph I

Monthly Average Values for the Amount of Fatty Acid Complex.

which the accumulated deficiency of rainfall was more than 10 inches, is accompanied by a falling tendency in the caoutchol curve. Supplementary data obtained prior to June, 1936, are indicated by the dotted section of the caoutchol curve. There is no indication of any relationship between the caoutchol content of latex and the wintering period.

Phosphate Complex.—No variations in chemical or physical character of this component from specimen to specimen were detected during the 12-month period. Samples invariably consisted of an amber-colored, pleasant-smelling, glassy material, which took up water and formed large crystalline plates (cf. Plate IC) when kept in open air.

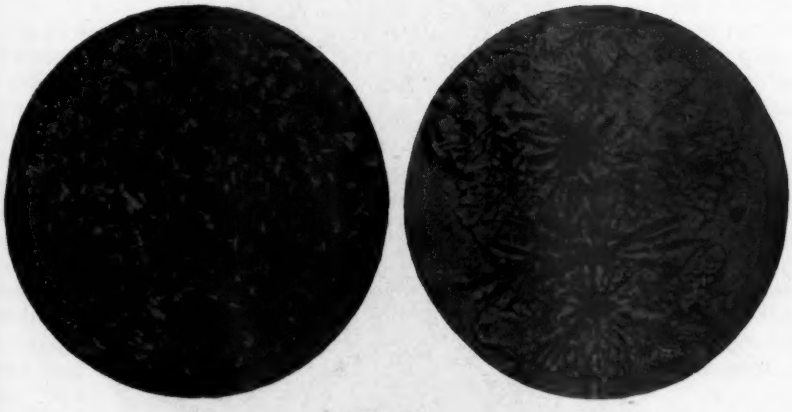


Graph II

Comparison of Caoutchol-Content of Latex with Rainfall

The extreme range of amounts of the complex (3.54–6.23 per cent of latex total solids) is considerable, but of the 42 specimens prepared, only three lay outside the range 4.0–6.0 per cent. It may therefore be stated that, for a component of a biological fluid, the phosphate complex shows a considerable degree of uniformity, both

A



B C

Plate I

A "Ammonium Salt" × 18
B Fatty Acid Complex × 18
C Phosphate Complex × 18

in character and in amount. Such variation as has been observed does not appear to depend on any of the factors considered.

Crude Rubber Hydrocarbon.—The specimens of this material prepared during the analyses were very uniform in character, all being plastic, amber-colored materials (cf. Plate IIA and B) having very slight elasticity and varying degrees of tackiness.

A

B

Plate II

A. Rubber Hydrocarbon, Freshly Prepared
B. Rubber Hydrocarbon, Kept 4 Weeks

Since the amounts of all components are expressed as percentages of the total solids of latex, the variation in amount of the hydrocarbon is naturally a reflection of the varying amounts of the non-hydrocarbon components. No evidence has been obtained that the properties of plantation rubber depend on the water content of latex.

Discussion

At the outset it is emphasized that the above is to be regarded as a preliminary study of this complex and important subject. It will be appreciated that it is very difficult to form conclusions from a study of analytical results which are likely to be influenced by a considerable number of variables. At the commencement of this work it was realized that under the best conditions then available it would be impossible to avoid possible variation, due to the drawing of the latex from an area of several hundred acres. This involved taking specimens from a wide range of soil and tree types, and from land having a varied topography. Also, with Malaya's heavy and very unevenly distributed rainfall, accurate correlation of analytical results with rainfall over such a large area was out of the question.

But in addition to the above possible sources of variation owing to other than seasonal causes, a number of other abnormal factors have been unavoidably introduced. These are enumerated below:

1. The period chosen has proved to be a phenomenal one climatically. A succession of months (February–May, 1936, inclusive) in which the rainfall greatly exceeded the average for those months (the accumulated excess rainfall was 13.96 inches), was followed by a period of seven months during which, with one exception, rainfall below the average for those months was recorded. The accumulated deficiency during this period was 10.54 inches (cf. Graph II). The ensuing four months, on the other hand, were all unusually wet, the accumulated excess rainfall for this period being no less than 20.22 inches. Such conditions are without parallel in the records of the past twelve years, and naturally cannot be expected to reflect the normal variability of the composition of latex. They have, however, had the advantage of revealing a relation between rainfall and latex composition which would otherwise have been less obvious (cf. Graph II).

2. The selection of the estate from which to draw latex samples, necessarily restricted by the need for obtaining specimens fresh from the field, has from the present point of view been unfortunate. The tapping system has been changed from time to time, and the analyses discussed represent samples drawn on daily, third-daily, and fourth-daily tapping systems. Further, from the above and other untraced causes, the dry-rubber content of latex samples dealt with has shown an extraordinarily wide variation (from 28.8 to 47.5 per cent). Although this is disconcerting from the point of view of this investigation, no evidence has been obtained that the composition of the total solids depends on the water content of latex.

3. Finally, the fire which practically destroyed the Chemical Division of the Institute caused considerable dislocation of certain aspects of the work for some time. A further investigation under conditions eliminating all variations of external factors except the climatic is in progress. The results to date confirm the above findings.

Conclusions

The investigation reveals that certain latex components are subject to wide variations, both in quality and in quantity, and that these variations are either in-

herent in the tree or are caused by external factors, chiefly rainfall, wintering, and refoliation, over which the producer has no control. The results of investigations of the effects on latex composition of the controllable factors, tapping system and genetic strain of the tree, will be reported in due course.

The observed variations in amount of two of the major non-caoutchouc components, *viz.*, the fatty acid complex and crude caoutchol, are judged to be large enough to cause variations in the physical and mechanical properties of plantation rubber. Variations of the phosphate complex on the other hand, appear unlikely to be significant from this point of view. The large variations shown by the minor components, ammonium salt and ester, are probably without technical interest, but it is suggested that they are closely associated with latex metabolism.

Summary

1. During a 12-month period, latex from a particular estate has been analyzed, as frequently as circumstances permitted, by the method already described.

2. All components show considerable and almost daily variations, which in the cases of the fatty acid complex and crude caoutchol are judged large enough to be of technical significance.

3. In addition to daily variations, two seasonal changes have been detected. In the first place, monthly average values of the amount of fatty acid complex reached a minimum during the wintering period, and rose immediately afterwards to a maximum coincident with refoliation. Secondly, monthly average values of the amount of crude caoutchol showed a rising or a falling tendency according as the rainfall was abnormally high or low over extended periods. These findings are receiving confirmation from a further series of observations made under the more rigorously controlled conditions now possible.

Acknowledgment

I am indebted to Hoh Choo Chuan for assistance in the preparation of the plates and diagrams.

Part III. Analyses of Plantation Rubber and of Creamed Latices

Introduction

The method of analysis of fresh latex described in Part I of this series (cf. Roberts, *J. Rubber Res. Inst. Malaya*, **7**, 46 (1936); RUBBER CHEM AND TECH., **10**, 1 (1937)) has been applied with only slight modifications to a variety of types of plantation rubber and creamed latex. It is also applicable to ammoniated latex, but since the composition of this product presents numerous special features, it is discussed in a separate paper, Part IV, which follows immediately.

Procedure

Rubbers.—The finely divided dried sample (30 g.) was added to a mixture of carbon tetrachloride (700 cc.) and acetone (450 cc.), and intermittently stirred until a homogeneous dispersion resulted. The remaining operations were carried out in the usual way.

Creamed Latices.—The cream was diluted with water to a rubber content of ap-

proximately 30 per cent, and the total-solids content of the product was determined. Fifty cubic centimeters of this liquid were dried on each of two of the standardized plate-glass frames, and the resulting film was treated in the normal manner.

Results

Tables I and II summarize analyses of a variety of typical samples of plantation rubber and creamed latex. The limits of the amounts of each component found in fresh latex to date are included in Table II for comparison. All findings are expressed as percentages of total solids.

TABLE I

COMPOSITION OF VARIOUS TYPES OF PLANTATION RUBBER

Component	Smoked Sheet	Pale Crepe	Water-White Crepe	Air-Dried Sheet	Crepe from Centrifuged Concentrate
Ammonium salt	0.004*	0.004	0.03	0.15	
Ester	0.08*	0.07	0.09	0.50	1.24
Fatty acid complex	1.53*	1.89	1.75	2.46	
Crude caoutchol	3.50	2.07	3.23	3.82	2.29
Phosphate complex	0.20	0.38	0.24	0.22	0.36
Hydrocarbon	94.20	95.20	94.04	92.23	...
Total	99.514	99.614	99.38	99.38	...

TABLE II

COMPOSITION OF VARIOUS TYPES OF CREAMED LATEX

Component	Triple-Centrifuged Cream	Tragon Seed Cream	Konnyaku Cream	"Synthetic" Cream	(Fresh Latex)
Ammonium salt	0.12	0.09	0.12	1.88*	0.00–0.23
Ester	0.28	0.36	0.18	0.43*	0.04–0.60
Fatty acid complex	1.49	1.59	1.97	2.01*	1.11–2.46
Crude caoutchol	4.40	3.90	3.96	3.47	1.25–4.66
Phosphate complex	0.63	0.74	1.20	1.31	3.54–6.23
Hydrocarbon	...	92.12	91.89	...	84.7–93.7
Total	...	98.80	99.32	...	.....

Discussion

1. All the components of fresh latex occur in each of the above products derived from it. The figures with asterisks represent components which consist in part of foreign matter acquired in the process of preparation.

2. Of the non-hydrocarbon components, the phosphate complex alone shows values which lie outside the limits observed for fresh latex (the special case of the ammonium salt of the "synthetic" creamed concentrate is discussed below).

3. The amounts of the water-soluble phosphate complex are all considerably lower than those found for fresh latex. This is the natural consequence of the fact that the serum solids which constitute the bulk of the phosphate complex are, to a large extent, removed in the sera during preparation of all the above specimens.

4. It is noteworthy that, although water-soluble, the ammonium salt appears nevertheless in normal amounts. It must therefore be associated in latex with another component in such a way as to be retained by the rubber-phase during the preparation of raw rubbers and creamed latices.

Smoked Sheet.—The ammonium salt of smoked sheet includes a small amount of a simple phenol (guaiacol or a cresol) derived from the smoke. It was detected by

its odor and by the development of a green color with ferric chloride. More complex phenolic substances from the smoke, similarly detectable, occur in the ester and the fatty acid complex. The caoutchol isolated was unusually tacky, the hydrocarbon was normal.

Pale Crepe and Air-Dried Sheet.—Apart from their low content of phosphate complex, these materials provided components indistinguishable from those of fresh latex.

Water-White Crepe.—The analysis closely resembles that of pale crepe. This observation is of particular interest, since this superfine grade of crepe is prepared by a process of fractional coagulation, which might be expected to remove, at least partially, certain of the major non-hydrocarbon components. It was noticed, however, that all the components isolated were unusually light in color.

Crepe from Centrifuged Concentrate.—This specimen of crepe was prepared by coagulation of diluted ammoniacal concentrate with magnesium silicofluoride, and soaking of the resulting coagulum before machining. It was less readily soluble in benzene and in carbon tetrachloride than normal rubber, and remained incompletely dispersed by the usual carbon tetrachloride-acetone mixture, even after 72 hours. The caoutchol isolated was very tacky, while the hydrocarbon was not easily soluble in rubber solvents. These are characteristic features of all rubber derived from ammoniated latex, and are discussed in the ensuing paper.

Triple-Centrifuged and Tragon-Seed Creamed Concentrates.—Quantitatively, these materials present no unusual features. The drastic washing action involved in their preparation resulted in the isolation of unusually light-colored non-hydrocarbon components. The effect of ammoniation was seen in the tacky texture of the crude caoutchol and in the increased resistance to solvents of the hydrocarbon.

Konnyaku-Creamed Concentrate.—The analysis of a cream prepared by addition of Japanese Konnyaku meal to ammoniated latex presented no additional features.

"Synthetic" Creamed Concentrate.—The creaming agent used in the preparation of this material was a proprietary substance, appreciably soluble both in water and in acetone. It is used in much larger quantities than the above two vegetable creamers, and appreciable quantities of it are therefore retained in the concentrate. Its solubility caused it to appear among the non-hydrocarbon components, as shown in Table II. The characteristics of the caoutchol and hydrocarbon fractions corresponded with the fact that no ammonia was used in the creaming process; that is, they resembled the corresponding products from fresh latex.

Summary

1. The method described in Part I of this series for the quantitative separation of the components of fresh latex has been applied to plantation rubber and creamed latices.

2. Quantitatively, the water-soluble phosphate complex alone among the components of raw rubber and creamed latices differs from the values found for fresh latex. The low values observed for this component reflect the removal of the serum solids in the different processes of preparation.

3. Qualitative differences from the components of fresh latex are of two kinds only:

(*a*) those due to occasional inclusion of foreign substances introduced during manufacture;

(*b*) those due to chemical changes produced in certain components by the action of ammonia.

Part IV. The Effect of Ammoniation on Latex

It is widely recognized that the preservation of Hevea latex with ammonia produces profound changes, but up to the present time investigation of the ammoniated product has been very largely restricted to observations of its physical properties—viscosity, surface tension, electrical conductivity, hydrogen-ion concentration, and so on (cf. Porritt and Dawson, "Rubber: Physical and Chemical Properties," Croydon, 1935, pages 6, 7, 8, 11, 15).

There are two reasons for the lack of chemical studies. In the first place, the absence of a method for the isolation of the individual components has rendered it impossible to correlate differences in the physical properties of latex with changes in any particular component; in the second place, fresh latex is, in the nature of things, not available in the laboratories of North America and Europe, with the consequence that comparison of the characteristics of fresh and preserved specimens of the same latex is not possible there. The first point has now been met by the development of the method of analysis described in Part I of this series (cf. Roberts, *J. Res. Inst. Malaya*, 7, 46 (1936)); RUBBER CHEM. AND TECH., 10, 1 (1937)), and the second, by applying the method to the study of ammoniated latex in one of the countries of production. An exhaustive comparative study of fresh and ammoniated latices from the point of view of acetone extract, acid value, surface tension, viscosity, and stability is now being made in these laboratories by E. Rhodes. This investigation should prove complementary to the present work.

Latex preserved by addition of 0.7 per cent by weight of gaseous ammonia may be prepared for analysis in almost the same way as fresh latex. Owing to the reduced viscosity of the treated material, a volume of only 50 cc. (instead of 100 cc. as for fresh latex) is distributed over each of the plate-glass frames preparatory to drying as usual. A slight modification of the analytical procedure is necessitated by the lowered solubility of rubber from ammoniated latex. The dispersion of the dried material in the carbon tetrachloride-acetone mixture is incomplete in the period of 24 hours which amply suffices for the total solid matter of fresh latex, and in order to assure complete removal of soluble non-hydrocarbon components by the dispersing medium, the mixture is kept before further treatment for a period of days, depending on the age of the latex. Even so, the ammoniated product, though finely disintegrated, remains on occasion incompletely dispersed.

Ammoniated latices examined have been of two types—ammoniated estate latices which had been stored for some months in metal drums treated internally to prevent discoloration of the latex, and laboratory specimens kept in glass vessels after ammoniation. The latter thus differed from the former in being exposed to the action of light. No evidence has, however, appeared that diffuse daylight itself has any effect on the latex components. Only with the laboratory specimens has it been possible to compare analyses with those of the same latex before preservation. Typical results are summarized in Table I later. In all the preserved samples, the ammonia content was approximately 0.7 per cent by weight of the latex.

Ammoniation produces such extensive changes in the majority of the components that the usual nomenclature becomes inapplicable, and it has been necessary to describe the materials isolated in more general terms. Thus the "fatty acid complex" is in the present connection called "ligroin-soluble matter;" crude caoutchol becomes "acetone-insoluble non-caoutchouc matter" and the phosphate complex, "water-soluble matter." The major component, isolable in a less pure form than from fresh latex, is called the "crude hydrocarbon."

Quantitative changes resulting from ammoniation do not appear to have any

particular significance in the case of ammonium salt, ester, and ligroin-soluble matter. The increase in amount of acetone-insoluble non-caoutchouc matter and the decrease in amount of water-soluble matter are however notable, and have been repeatedly observed.

The only components which are not profoundly changed qualitatively by ammoniation are the two minor ones, ammonium salt and ester.

The *fatty acid complex* of fresh latex, composed of a considerable number of alcoholic and acidic substances in chemical combination, is extensively hydrolyzed under the conditions of ammoniation, and is isolable as a corresponding ligroin-soluble mixture of the individual components of the original complex, *viz.*, alcohols, aliphatic acids, glucoside and terpenic substances. This has been established by comparing the behavior of the two types of ligroin-soluble matter under the action of alcoholic caustic soda.

TABLE I

Constituent	Laboratory Specimens: Fresh	Laboratory Specimens: Ammoniated (No. of Weeks in Parentheses)		Commercial Latex Ammoniated 18 Months
Ammonium Salt	0.09	0.09	(8)	
+ Ester	0.30	0.36	(4)	0.42
		0.24	(14)	
Ligroin-soluble matter	1.13	1.12	(8)	
	1.76	1.81	(8)	1.41
		1.73	(18)	
Acetone-insoluble	2.54	7.25	(8)	
non-caoutchouc matter	3.10	7.07	(18)	7.42
Water-soluble matter	5.58	3.93	(4)	
		3.53	(8)	3.22
		3.22	(18)	

The *phosphate complex* suffers a similar change. The naturally occurring material contains, among other things, mineral phosphates, a reducing sugar, and quebrachitol, but owing to their state of combination, it does not give characteristic reactions for these components. The corresponding "water-soluble matter" from ammoniated latex, on the other hand, gives reactions for all three.

The *crude caoutchol* of fresh latex is in general an elastic substance; the corresponding "acetone-insoluble" component of ammoniated latex, however, is invariably a highly viscous fluid, extremely tacky and possessing no elasticity.

The *hydrocarbon* component also undergoes a fundamental change during ammoniation. The hydrocarbon isolated from ammoniated latex showed a much greater resistance to solvent action than either raw rubber or hydrocarbon from fresh latex.

The above extensive changes in the character of the major components of latex under the action of dilute aqueous ammonia are effected within a period of eight weeks, and will thus be far advanced before ammoniated latex reaches the consumer.

The most critical changes from the point of view of the properties of rubber are undoubtedly those involving the caoutchol and the hydrocarbon components. Specimens of these substances, isolated from fresh latex in their naturally occurring forms, have accordingly been independently subjected to the action of dilute aqueous ammonia, with a view to elucidating the nature of the changes.

Crude caoutchol (20 g.) isolated from 2 liters of fresh latex, was added in the form of a thin sheet to distilled water (2 liters) containing 0.7 per cent by weight of am-

monia, and the mixture was kept for eight weeks, with intermittent shaking. In this way the concentrations and storage period for typical commercial ammoniated latex were closely imitated. At the end of the period, the aqueous liquor remained clear, but had become yellow. From it was isolated a small amount of a complex mixture of organic acids, including the sulfur-containing component of crude caoutchol mentioned in Part I (2). It is concluded that dilute ammonia exerts a hydrolytic action on crude caoutchol. The insoluble portion of the reaction mixture had during eight weeks become opaque, cream-colored, and spongy by absorption of the medium. After being washed with water, milled, and dried *in vacuo*, it was a tough, translucent material insoluble in ether and only very slowly dissolved by the usual rubber solvents—behavior very different from that of the untreated substance. Caoutchol so modified will necessarily be retained by the hydrocarbon on analysis. The change is apparently one of polymerization.

The hydrocarbon from fresh latex, treated in a manner similar to the above, likewise became a soft opaque mass, but no portion of it was dissolved by the ammoniacal medium. The washed product, milled to a thin sheet and dried *in vacuo*, was a tacky, light brown substance which was only slightly dissolved in 3–4 hours by the usual rubber solvents. The undissolved portion slowly swelled in the solvents, but even after 24 hours it remained largely undissolved by benzene, carbon disulfide, ether, and ligroin. A higher degree of dispersion was observed in chloroform, carbon tetrachloride, and toluene, but in these media also, solution was incomplete. The untreated hydrocarbon, on the other hand, dissolves readily with but little swelling. It is suggested that the soluble portion of the treated hydrocarbon is a disaggregated form, which, being more soluble than the normal form, is retained by the carbon tetrachloride-acetone mixture during analysis, and appears as the "acetone insoluble matter" in place of caoutchol. The insoluble portion, which constitutes the bulk of the treated product, appears to be a polymer of the naturally occurring hydrocarbon.

These relationships throw light on the apparent loss of water-soluble substances indicated in Table I. The procedure which suffices for the quantitative removal of water-soluble substances from the total solids of fresh latex is inefficient when applied to the ammoniated product. An appreciable amount of inorganic material is retained, along with modified caoutchol, by the crude hydrocarbon, and may be readily detected as ash.

Summary

1. Comparative analyses of fresh and ammoniated latices have been made, and the components investigated.

2. The changes effected by ammoniation are profound, and are far advanced in a period of eight weeks. Only the minor components, ammonium salt and ester, are inappreciably affected.

3. The fatty acid and the phosphate complexes of fresh latex undergo extensive hydrolysis within eight weeks of ammoniation, and part of the inorganic matter is firmly retained by the modified hydrocarbon. (See 5 below.)

4. The crude caoutchol of fresh latex is replaced by an increased amount of a viscous fluid which is thought to consist of a disaggregated portion of the hydrocarbon. Caoutchol itself, treated with dilute aqueous ammonia, becomes relatively insoluble, and is presumably retained on analysis by the remainder of the hydrocarbon.

5. The hydrocarbon of fresh latex is replaced by an ash-containing material which has a marked resistance to solvent action. This latter property is due not

only to retention of the modified caoutchol (4 above), but also to modification (polymerization ?) of the hydrocarbon itself by the action of the ammonia.

Acknowledgments

I wish to express my thanks to S. A. Nathan and K. H. Rajagopal for their assistance with the analytical work involved in this and the two preceding papers, and my indebtedness to E. Rhodes for much helpful discussion and advice.

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The Preparation of Latex and Determination of Quality

W. S. Davey and F. J. Coker

Latex production has steadily increased during the last few years, as shown by the figures in Table I, which have been extracted from data published by the International Rubber Regulation Committee.

Since 1934, output has nearly doubled, and for this year it is estimated, from the average figures for the first nine months of the year, that it will amount to approximately 35,000 tons. No statistics are published as to the respective amounts of preserved field latex and concentrated latex which comprise this 35,000 tons, but assuming the latex to contain an average of 50 per cent dry rubber, this quantity would represent approximately 16,000,000 gallons. Almost the whole of this latex is exported from Malaya and the Netherlands East Indies, only a negligible quantity being shipped from other rubber-growing countries. This production is confined to relatively few estates and in this respect affords a strong contrast to the production of estate rubber in the form of sheet or crepe, which is spread over many estates and small holdings (in Ceylon alone it is computed that rubber is produced on 100,000 estates and small holdings, mostly the latter). Latex production must of necessity be limited to the larger estates for both technical and commercial reasons, as the smallest consignments which are conveniently handled by European importers are around 500 gallons, and for some estates even the production of this quantity entails bulking several days' crop. On the other hand, some large estates export regularly 20,000 gallons or more every month, and the practice is growing of bulking supplies from individual small estates at central factories.

A well-known firm of latex brokers described, in their monthly review, the shipment and marketing of latex as a "highly specialized matter which should not be undertaken lightly," and proceeded: "in the past some estates have sent latex home unsold, and have been disappointed with the results. Sometimes the latex has been improperly prepared and has turned a bad color, or in some cases it has coagulated. In some cases it has been held in store too long hoping for a better market. Having been once bitten, these companies, and others who have heard of their experience, are shy of trying further shipments in this form." The views expressed in this paragraph indicate two important facts in connection with latex production: first, that it is dangerous to embark on latex production without some reasonable assurance of a market for the product, and second, that it is essential to produce a good quality material in order to obtain and subsequently retain that market. Generally contact between the producer and importer of latex is closer than that between the producer and user of rubber in the form of sheet or crepe. The latter can be produced in the certain knowledge that it will eventually find a purchaser, but with latex there is not an entirely free market.

It is generally admitted that the quality of latex has improved during the last few years, which is considered to be due largely to the knowledge gained from the investigations made of the factors affecting quality by officers attached to the research organizations in the East.

Rhodes and Sekar (*J. Rubber Res. Inst. Malaya*, **5**, 176 (1934)) made a systematic

study of the causes of the discoloration of latex, because "so much importance is now attached to the characteristic of color that the suppliers who have been fortunate in establishing a reputation in European and American markets for the production of latex which reaches its destination in a good white condition have earned for themselves an assured market, whereas many of those whose products were not until recently made the subject of complaint have either lost or are in danger of losing their market."

TABLE I

EXPORTS OF LATEX FROM PRINCIPAL PRODUCING COUNTRIES, 1931–1937

Year	Dry Rubber Content (Tons)
1931	5,817
1932	8,683
1933	18,731
1934	19,505
1935	20,914
1936	28,494
1937 (first 9 months)	26,492

Rhodes and Sekar considered the possibility of the discoloration of latex being due to the presence of oxidizing enzymes such as tyrosinase, which causes the darkening of pale crepe, but they could find no correlation between the extent of the discoloration and the varying enzyme activities of the latices examined. They proceeded to demonstrate very conclusively that discoloration was due to the interaction of soluble sulfur compounds and iron salts, with the formation of iron sulfide in a colloidal condition. In the absence of both the components necessary for this reaction, it was observed that no discoloration occurred. In connection with this, Roberts (*J. Rubber Res. Inst. Malaya*, **7**, 46 (1936)) has recently shown that sulfur compounds are invariably present in latex, his so-called sulfur complex amounting to as much as 0.92 per cent of the latex (2.4 per cent based on the solid content). In ammoniated latex this complex is largely hydrolyzed into soluble sulfur compounds, which are therefore invariably present in latex and in such a condition as to be capable of reacting with iron salts. The latter are not initially present in latex to any appreciable extent, and the problem therefore resolves itself into taking the necessary steps to prevent their entry through contamination with iron vessels, settling and storage tanks and the containers in which the latex is subsequently shipped.

TABLE II

GROWTH OF BACTERIA IN FRESHLY TAPPED UNPRESERVED LATEX

	Per Ml.
At 11.15 A. M. latex gave a bacterial content of	6,000,000
At 11.30 A. M. latex gave a bacterial content of	60,000,000
At 1 P. M. latex gave a bacterial content of	400,000,000
At 2 P. M. latex gave a bacterial content of	2,000,000,000

It was also shown that discoloration was much more pronounced in latex which was allowed to putrefy before adding the preservative. Putrefaction depends entirely on the growth of bacteria, which in the case of fresh unpreserved latex proceeds at a rapid rate, as it contains sugars and proteins which are essential for the promotion of their growth. This is illustrated in Table II which shows the results of the bacterial determination made on a freshly tapped latex from which cultures were grown on dextrose agar and counts taken at intervals (Beeley, Rubber Research Institute of Malaya, *Annual Report, Pathological Division*, **1934**).

This bacterial activity always proceeds with the formation of acidity, consisting chiefly of lactic and butyric acids, which readily attack iron. Therefore, any delay in adding ammonia after tapping enhances the possibility of the latex being contaminated when in contact with iron. On the other hand, even if the latex is ammoniated promptly, contamination in contact with iron proceeds, although much more slowly. In order to demonstrate these effects, a series of samples of latices has been prepared by Hastings (Rubber Research Institute of Malaya) and the color examined in London by means of the Lovibond Tintometer. The results of these determinations are shown in Table III.

TABLE III

EFFECT OF DELAYED AMMONIATION ON THE DISCOLORATION OF LATEX BY IRON

Color determined by Lovibond Tintometer

	Series A In Contact with Iron for 4 Days after Tapping			Series B In Contact with Iron Continuously					
	Observer A			Observer A			Observer B		
	Blue	Yellow	Red	Blue	Yellow	Red	Blue	Yellow	Red
Control	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.0	0.1
Control + iron	0.4	0.1	0.1	0.3	0.1	0.0	0.4	0.0	0.1
Addition of ammonia delayed for:									
½ hour	0.5	0.1	0.1	0.6	0.1	0.2	0.8	0.1	0.2
1 hour	0.5	0.2	0.1	0.9	0.2	0.2	1.0	0.2	0.1
2 hours	0.7	0.2	0.1	0.7	0.2	0.2	0.8	0.1	0.2
3 hours	0.6	0.1	0.2	0.9	0.2	0.2	0.9	0.1	0.2
4 hours	0.7	0.2	0.2	0.8	0.2	0.2	0.9	0.1	0.2
5 hours	0.8	0.2	0.2	0.9	0.2	0.2	0.9	0.1	0.2

It is obvious therefore that, as a result of this work, addition of ammonia to latex as soon as possible after tapping is essential, contamination with iron vessels should be avoided, and all vessels should be kept clean, in order to avoid unnecessary bacterial contamination.

For many years 0.5 per cent ammonia was considered to be sufficient for the sterilization of field latex, but it was subsequently found that this quantity did not prevent periodical outbursts of bacterial activity in a minority of latices, whereas a larger amount (0.7 per cent) was effective in all cases In order to allow a margin of safety the use of this larger amount has been recommended (Rubber Research Institute of Malaya, *Annual Report, Chemical Division*, 1934).

Bishop and Fullerton ("Latex Preservation and Shipment," D8, 1932) remark that during storage a gradual decrease in ammonia content takes place, and give an example of a latex in which the ammonia fell from 0.50 per cent to 0.47 per cent after 1 week, to 0.45 per cent after 1 month, and to 0.20 per cent after 2 years. This is evidently an example where 0.5 per cent ammonia did not produce sterility, and hence cannot be taken as typical of the behavior of latex. It is found from samples which have been under observation for nearly a year that if the latex is properly sterilized little change in ammonia content occurs. This is illustrated by the results shown in Table IV, in which four samples of latex drawn from the same bulk and ammoniated to different degrees were examined 12 months after preparation.

The four latices show a slight decrease in rubber content on keeping for 12 months, probably due to the formation of small lumps of coagulum. The ammonia content shows that no marked changes have taken place.

In order to illustrate the extent to which the recommendation of the Rubber Research Institute of Malaya is being carried out, Fig. 1 shows the distribution curve of the ammonia contents of 61 samples of preserved field latex drawn from various

commercial consignments. By far the greater proportion of the samples lay in the region 0.60–0.70 per cent; none had an ammonia content of less than 0.5 per cent, but on the other hand, one sample contained 0.8 per cent and two samples over 1.0 per cent. The addition of excessive amounts of ammonia does not confer any advantage on the latex; on the contrary, as will be observed later, it tends to have an adverse effect as regards stability on keeping.

TABLE IV

CHANGES IN LATEX DURING STORAGE

Sample	Dry Rubber Content		Ammonia Content	
	Original Determined in Malaya	After 12 Months' Storage in England	Original Determined in Malaya	After 12 Months' Storage in England
L. A. C. 15	36.5	36.3	0.56	0.50
L. A. C. 16	36.2	35.8	0.77	0.79
L. A. C. 17	36.0	35.4	1.24	1.19
L. A. C. 18	36.0	35.6	1.64	1.58

Preservatives other than ammonia have been used from time to time by special arrangement between buyer and producer. Although ammonia, owing to its volatility, is considered the best preservative at present available for latex which is to be used in the rubber industry, other preservatives are probably more suitable for latex which is to be used in other industries. A case in point is in the use of latex for plastic rubber flooring, which was described by Wren (*Trans. Inst. Rubber Ind.*, 13, 189 (1937)); here the evolution of ammonia which occurs during the addition of the cement owing to the presence of lime is very unpleasant for the work-people.

The need for a satisfactory alternative non-alkaline preservative is realized by the research organizations, and many sterilizing agents have been examined, but up to the present it has not been possible to recommend one which could be considered as absolutely satisfactory. The conditions which a bactericide has to fulfil are very exacting; it must not only be effective against bacteria but also must not have any ill effects on the latex as regards color, stability, etc., it should be non-toxic as far as possible and should be competitive as regards cost. Among the most promising of the materials so far examined are salts of arsenic and mercury, which of course are poisonous and therefore have to be ruled out. Claims are often made for the efficiency of proprietary materials as preservatives, but it seems that these are based on tests made with deammoniated preserved latex, as experience so far obtained with fresh latex shows that they invariably fail. Satisfactory tests of the efficiency of any preservative can only be made with fresh latex. With any non-alkali preservative, it will always be necessary to use a small amount of ammonia, otherwise the viscosity of the latex is too high for convenient handling, being comparable to that of a highly concentrated latex.

Up to the present, mention has been made briefly of some factors in latex production affecting the quality of the latex which can be carefully controlled, such as the nature and amount of preservative used, the period which elapses between tapping and addition of the preservative, cleanliness of the vessels and tanks through which the latex passes during its preparation on the estate, and the adoption of adequate means to prevent contamination with iron. There are, however, other important factors influencing the quality of latex which cannot be controlled (Rhodes, *Ind. Eng. Chem.*, 27, 1204 (1935)). The composition of latex depends on local conditions such as the nature of the soil and climate and on the trees themselves, their age and genetic strain. Tapping systems vary in severity in different

areas and countries; one estate may tap continuously every alternate day, another every third day, and yet another may tap daily continuously for one month and then rest for one month. Then there is the geographical position of the areas under tapping in relation to the central factory, the different types of transport available, both factors of which tend to produce variation in quality between different estates. On large estates many of these variations are removed by bulking, and experience seems to show that the variation in latex between different estates is larger than successive consignments from the same estate. Hence, a certain estate may gain a reputation for producing a latex of high stability, and some importers differen-

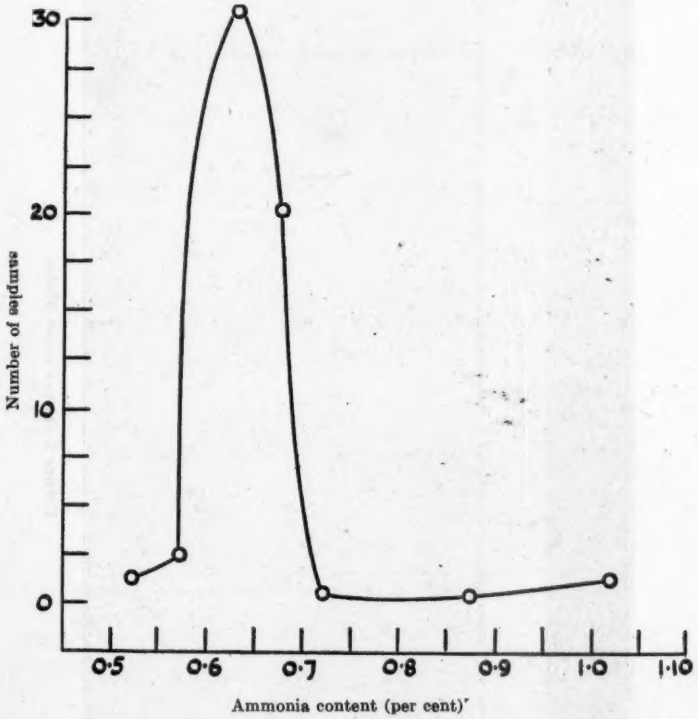


Figure 1—Distribution Curve of Ammonia Content of 61 Commercial Samples of 40 Per Cent Latex

tiate accordingly between the consignments they receive from different estates by allotting to manufacturers latex which will be most suitable for their requirements.

The precautions taken to prevent contamination by iron corrosion during the preparation of latex must also be observed in the containers used for its shipment. The provision of suitable containers has long presented a problem to producers, which has not been entirely solved by the method of exporting latex in bulk in tanks, this being available only to large producers with the necessary facilities. Further, there is the distributing end to be considered, where provision has to be made for supplying small amounts. The ideal container would be some form of non-corrosive steel material, but the cost is out of the question. Wooden barrels have

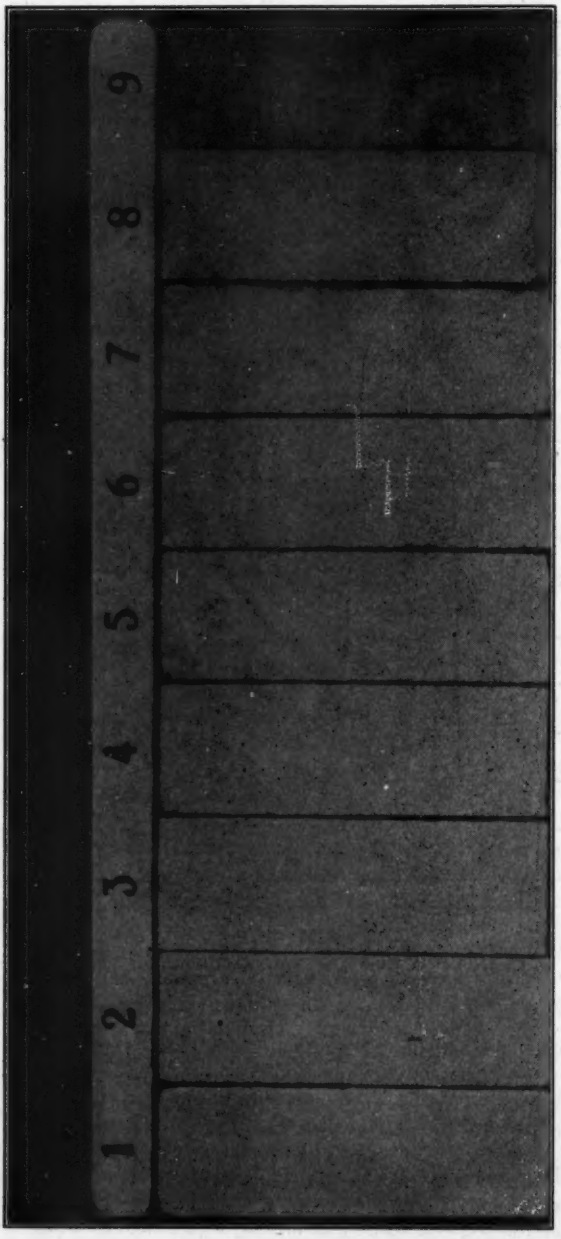


Figure 2—Latex Color Slides

been tested, but for various reasons these have not been used. Latex is still shipped to this country in kerosene tins, although they have disappeared from shipments to

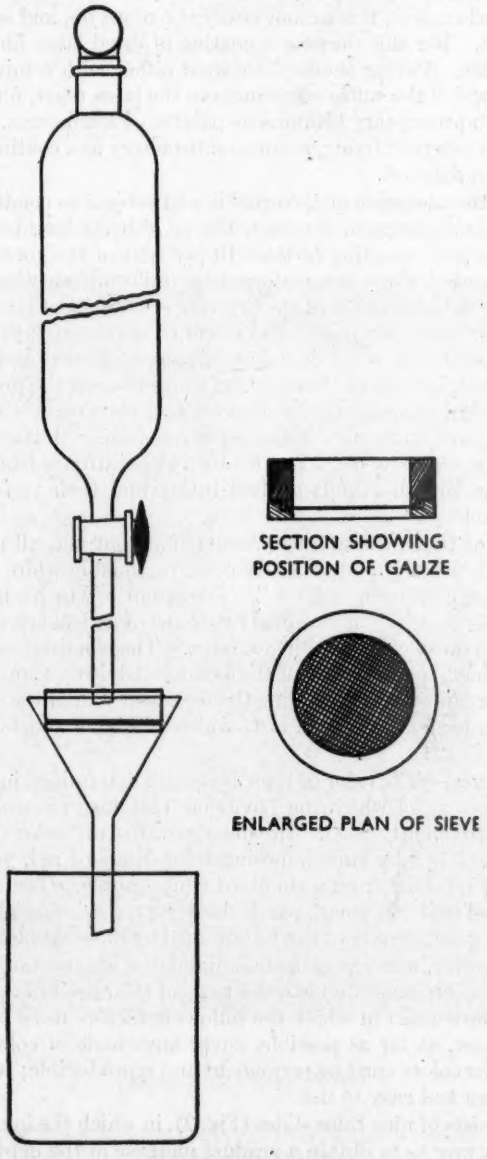


Figure 3

the United States, latex being exported to that country almost entirely in bulk or in drums.

Considerable work has been done by the Rubber Research Institute of Malaya

in coöperation with estates and importers in their effort to find suitable coating materials for the insides of latex containers. In the case of kerosene tins, if the tinning has been efficiently carried out, it should be sufficient to prevent contamination, but, unfortunately, this cannot always be relied on, and some form of treatment is desirable. For this purpose a coating of dried latex film has given fairly satisfactory results. Drums should be coated either with a mixture of latex and zinc oxide, with which the sulfur substances in the latex react, forming zinc sulfide, or preferably with proprietary bituminous paints. Paraffin wax, which apparently gives good results as a tank lining, is not so satisfactory as a coating for drums owing to its tendency to flake off.

All latex with the exception of Revertex is sold subject to conditions laid down in the Rubber Trade Association contract, the price being based on the dry rubber content, which entails sampling at least 10 per cent of the containers. Although it may appear belated, there is a real need for uniformity in the methods used for sampling and the determination of the dry rubber content of latex. Differences in technic may easily affect the result, and it will be appreciated that a small error in the dry rubber content of a consignment running to 30,000 or 40,000 gallons will amount to a considerable sum of money. Drums present the greatest difficulty in sampling, particularly as regards the dispersion of the cream which tends to form on concentrated latex, vigorous stirring being essential. Methods of sampling and analysis are at present under consideration by a Committee of Rubber Technologists appointed by the British Standards Institution and their recommendations will shortly be available.

By the terms of the Rubber Trade Association contract, all latex sold must be "completely fluid, free from putrefactive odor, reasonably white in color, and commercially free from extraneous matter." The extent to which a latex complies with these conditions is generally determined by means of a visual examination based on experience gained during the handling of latex. The conditions have not up to the present been defined, and the staff of the London Advisory Committee in coöperation with other organizations, including the technical staff of the Dunlop Company, has attempted to formulate certain tests which will be of assistance in the evaluation of latex.

1. *Color of Latex.*—The color of latex is readily determined in the laboratory by means of colorimeters, of which the Lovibond Tintometer is probably the type of apparatus most frequently used. In this apparatus the color of the latex by reflected light is matched by superimposing color-filters of red, yellow, and blue in the path of light reflected from a standard white source. The values obtained in terms of Lovibond units are small, particularly for a good colored latex, but despite the small values, good agreement can be obtained by different observers (Table III).

There are, however, many persons handling latex who do not possess the necessary colorimetric equipment, and in order to meet their needs a series of color standards has been constructed in which the following factors have been kept in mind: (*a*) the range must, as far as possible, cover any shade of color likely to be encountered; (*b*) the colors must be permanent and reproducible; and (*c*) the apparatus must be cheap and easy to use.

The series consists of nine color slides (Fig. 2), in which the ingredients have been graded in such a way as to obtain a gradual increase in the depth of color. They were prepared by using a basic mix of titanium oxide and cadmium sulfide with increasing amounts of lamp black, the mixture being cemented together with sodium silicate after smearing on microscope slides. The compositions of the colors, which are based on observations of the color of latices made with the Lovibond Tintome-

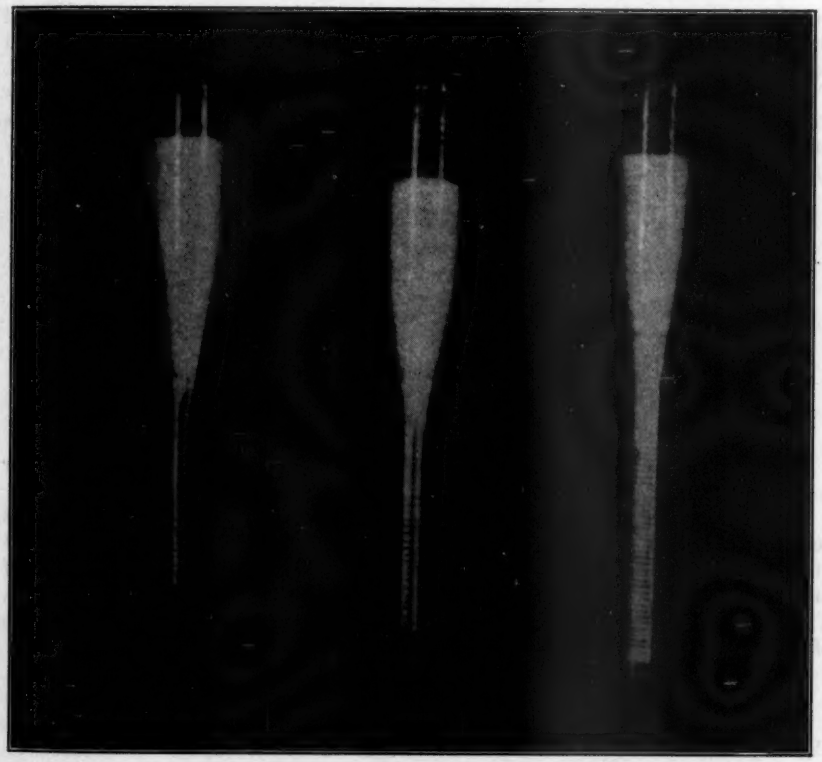
ter, are shown in Table V. It is anticipated that these colors will become available to the trade in the form of color cards.

TABLE V

BASIC MIX { TITANIUM OXIDE 100.00; CADMIUM SULFIDE 0.06 }

Slide No.	1	2	3	4	5	6	7	8	9
Lamp black (Parts per 100 parts of basic mix)	nil.	0.015	0.03	0.06	0.10	0.14	0.18	0.36	0.56

Occasionally one encounters latex of a yellow color obtained from certain clones or from an area which has just been brought into tapping. Although the color



Tube No. 1 Tube No. 2 Tube No. 3

Figure 4—Centrifuge Tubes

slides referred to may not match such a latex, they enable a classification to be made, which is the chief concern of the market as the evaluation of latex as far as the amount of dirty gray color is concerned governs the allowance which has to be made for an off-colored latex.

2. *Extraneous Matter, Coagulum, and Finely Divided Material.*—The presence of coarse material, such as extraneous matter, and coagulum and finely divided

material which settles out as a sludge, is of particular importance in the manufacture of fine grade articles, such as thread and dipped goods. Although latex is strained on the plantations and elaborate plants have been devised for settling out the sludge, commercial latex is never entirely free from undesirable material.

A disc of stainless steel gauze (80-mesh) clamped between two stainless steel rings, resting on a glass funnel, forms a very convenient sieve for straining out the coarse material (Fig. 3). Six hundred cc. of preserved field latex or 400 cc. of concentrated latex are poured into the separating funnel and diluted with sufficient distilled water containing 0.6 per cent of ammonia to give a latex with a dry rubber content of approximately 25 per cent. The latex is run slowly from the separating funnel through the weighed disc of stainless gauze, and the residue washed with distilled water containing 0.6 per cent of ammonia until free from latex. The gauze is then removed, the residue dried and weighed, and the results expressed as grams per liter of original latex. As the coarse material may not be evenly distributed throughout the bulk of the latex, it is important that the latex should be well stirred before taking a sample and that three separate samples should be taken and tested. Table VI shows some typical results. It will be observed that, although there is sometimes appreciable variation in the results given by different samples from the same latex, there are much greater differences between the average results given by different latices, showing that the test is of significant value.

TABLE VI

Experiment	Commercial 40 Per Cent Latex (Grams per Liter)	Latex Creamed with Special Creaming Agent (Grams per Liter)	Evaporated Creamed Latex A (Grams per Liter)	Evaporated Creamed Latex B (Grams per Liter)
1	0.057	0.432	1.21	1.36
2	0.017	0.675	1.38	1.04
3	0.010	0.478	1.10	0.96
Average	0.028	0.528	1.23	1.12

After use the stainless steel gauze is easily cleaned by warming in nitric acid for a short period, washing, and drying.

The finely divided material in latex may be estimated by a method based on that recently published (*Analyst*, 62, 287 (1937)) for the determination of the amount of dirt in milk. This consists in allowing dirt to settle out of a large volume of milk into standard centrifuge tubes and then compacting in a laboratory centrifuge. The standard centrifuge tubes (B. S. S. 736, 1937) are accurately calibrated and are of three sizes (Table VII, Fig. 4).

TABLE VII

	No. 1	No. 2	No. 3
Capacity of graduated portion	0.020 cc.	0.050 cc.	0.200 cc.
Sub-divisions	0.001 cc.	0.002 cc.	0.005 cc.
Lowest graduation	0.002 cc.	0.004 cc.	0.020 cc.
Approximate bore at graduated part	0.9 mm.	1.3 mm.	2.4 mm.

Latex contains a much higher proportion of sediment (up to 10 parts per 1000 by volume) than milk (1 to 10 parts per 100,000), and the preliminary settling out necessary in the case of the latter may be dispensed with in the case of latex.

In the determination of finely divided material, it is advisable to use all three tubes, as the amount may be too small for measurement in No. 3 tube and too large for No. 1. Tubes Nos. 1 and 2 will, however, generally be found to be most ap-

plicable. Two cc. of latex from which the coarse material has been removed are accurately measured into each tube and spun for 5 min. in a centrifuge, of such a size that the measurement of the machine, when in action, from the extreme ends of the whirling tubes is 10.5 inches, at a speed of 2000 revolutions per minute. It is advisable that the centrifuge should be motor-driven in order to obtain the exact speed of rotation. After spinning, the latex is poured off, replaced by ammoniacal

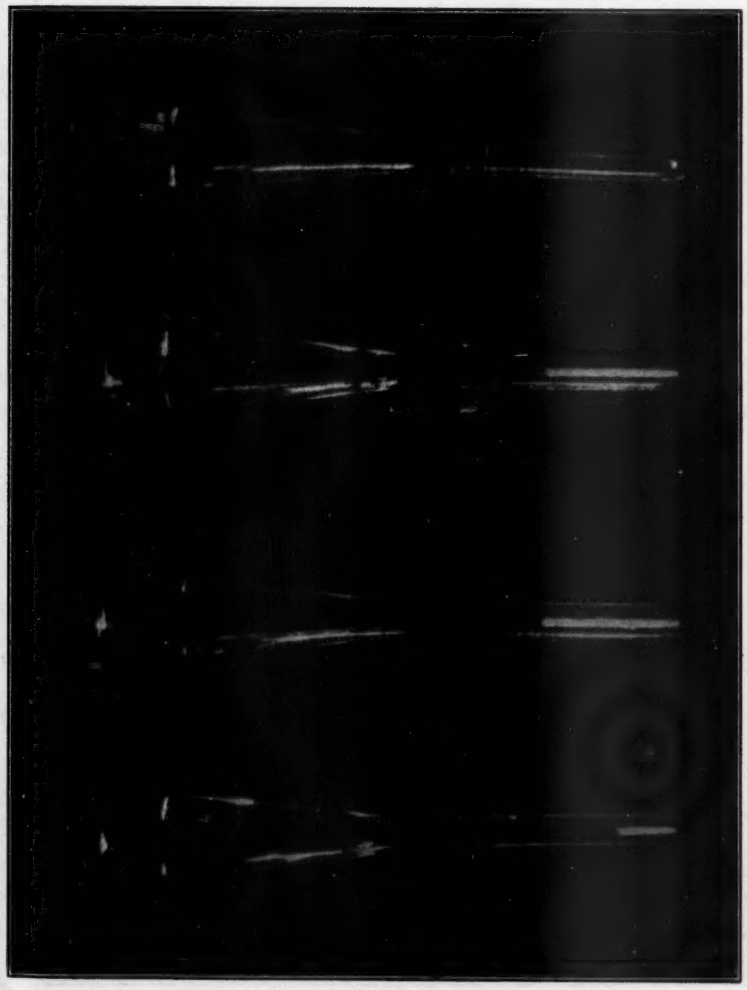


Figure 5—Deposits from Different Latices

water, the deposit stirred with a fine wire and centrifuged for 5 minutes. This is twice repeated and the residue measured and recorded as parts of moist residue per 1000 parts of latex. Typical results using No. 2 tube are shown in Fig. 5.

3. *Putrefactive Odor.*—Detection of any sign of putrefaction is one of the most important tests in the evaluation of latex because its effects can be so far reaching, but with the present knowledge of latex preservation there is no reason why latex

which is not properly sterilized should be shipped. Putrefaction in the early stages is not always easily detectable, the odor being masked by the preservative present. If, however, the latex is coagulated with a non-volatile acid, such as sulfuric or boric acid, the objectionable odor can be easily recognized. Van Dalfsen (*Arch. Rubbercultuur*, **21**, I(1937)) has put forward a method of identifying putrefaction based on

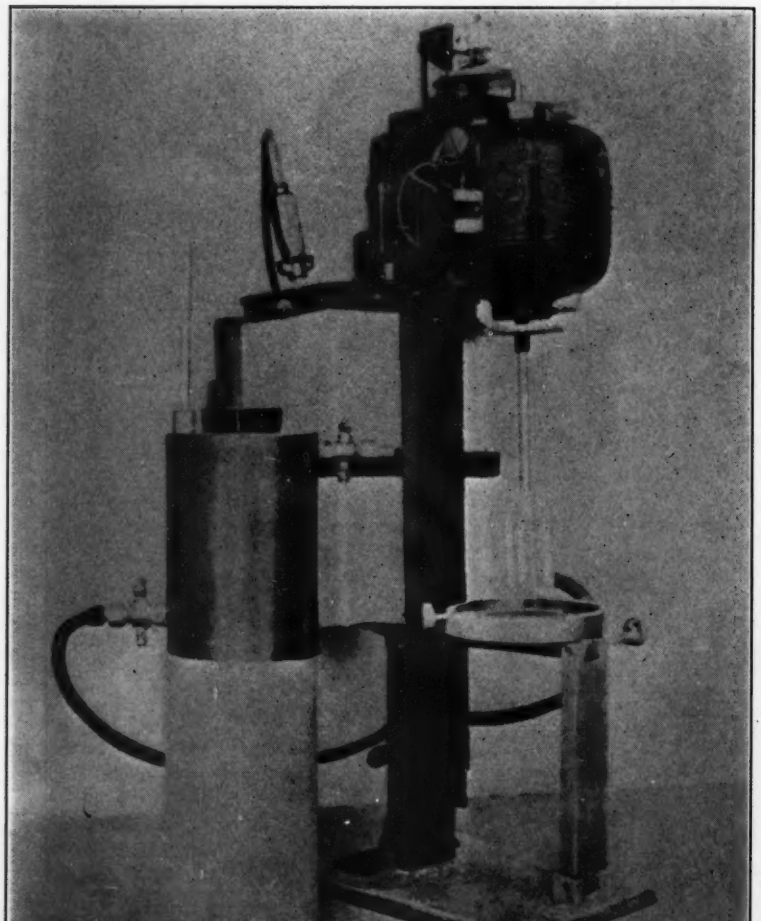


Figure 6—Stability Apparatus

the time necessary to reduce the color of methylene blue, claiming that bad latex gives a low decoloration time. Up to the present the authors have not had any success with this method; and there seems no simple method, chemical or otherwise, of identifying putrefaction, apart from the relation it bears to the stability of latex.

In addition to the desirable properties laid down by the Rubber Trade Association, the stability of the latex and the quality of the rubber are also of importance.

Stability.—The general conception of the stability of a latex is the measure of its ability to resist coagulation under the stress of mechanical or chemical forces. During the movement of latex from estate to factory, it is subjected to mechanical stresses which it must be capable of withstanding, and its capacity for doing this depends on the nature of the serum substances forming the protective coating on the individual particles and also on their electric charge, which in turn is related to the nature and efficiency of the preservative in preventing bacterial action. The coagulation of latex by rubbing on the hand, which is caused partly by frictional forces and partly by the removal of the water phase, is used by everyone handling latex as a means of testing its stability, and as a rough test serves a very useful purpose. In order to obtain a more accurate measurement of stability, tests have been developed in which the latex is subjected to violent agitation by mechanical stirrers, the time necessary to produce coagulation by the frictional forces involved being taken as a measure of the stability of the latex.

A form of apparatus used in America is a high-speed Hamilton Beach mixer. The apparatus is very compact, only a small amount of material being necessary, and the high speed of stirring (14,000 revolutions per minute) results in rapid determinations. On the other hand, the end-point, which is determined by noting when one drop of the latex under test coagulates on the surface of a layer of water, is somewhat indefinite, and the high rate of stirring causes frothing and overflowing with certain types of stabilized latices. The indefinite end-point is due to the necessity of having the stirrer in the form of a horizontal sinuous disc, which tends to break up the coagulum when formed, resulting in an end-point which is largely a matter of personal judgment. Some results obtained with this apparatus are shown in Table VIII in which 50 cc. of different latices, diluted to 30 per cent dry rubber content, were stirred at a speed of 14,000 revolutions per minute.

TABLE VIII

Sample	Time in Minutes to Reach End-Point
L. A. C. 15 (36.7 per cent latex)	3, 2.5, 2.5
L. A. C. 16 (36.3 per cent latex)	4, 3.5–4, 4
L. A. C. 17 (36.1 per cent latex)	5.75, 5.25
Revertex	Frothed badly over the top of the container
Centrifuged latex	Large lumps of coagulum formed in the latex
Old latex (40 per cent latex)	1.5

In order to overcome the difficulty of the indefinite end-point, Jordan, Brass, and Roe (*Ind. Eng. Chem., Anal. Ed.*, **19**, 182 (1937)) suggested inserting a milliammeter in series with the motor and noting the point when the reading shows a rapid rise in current consumption owing to complete coagulation of the sample.

With the apparatus used in the London Advisory Committee laboratories, a much lower speed of stirring is employed, and a fixed amount of zinc oxide based on the dry rubber content of the latex is added; this has the advantage of giving a definite end-point when coagulation takes place. The apparatus is shown in Fig. 6. It consists of a water-jacketed stainless steel container 6 × 2 inches diameter with a stirrer 2 inches long, having three vertical radial blades, 2 × $^3/_8$ inches, radiating from a central hub of $^{13}/_{16}$ inch diameter. The container is rigidly fixed, and the speeds of the stirrer used have varied from 600 to 2000 revolutions per minute. The number of revolutions required to cause coagulation is measured by means of a tachometer. Any stability test of the mechanical type is necessarily arbitrary,

and it is essential in order to obtain comparable results between different laboratories, not only to standardize the apparatus and the speed of stirring, but also (*a*) the quantity of latex of a fixed dry rubber content, (*b*) ammonia content, (*c*) amount of zinc oxide based on the dry rubber content, (*d*) type of zinc oxide, and (*e*) the temperature of testing.

The effect on the results of varying the amount of zinc oxide is shown in Fig. 7, which gives the results of the examination of five samples of latex comprising two samples of preserved field latex which had been stored for some months, a sample of freshly preserved latex, a creamed latex, and Revertex.

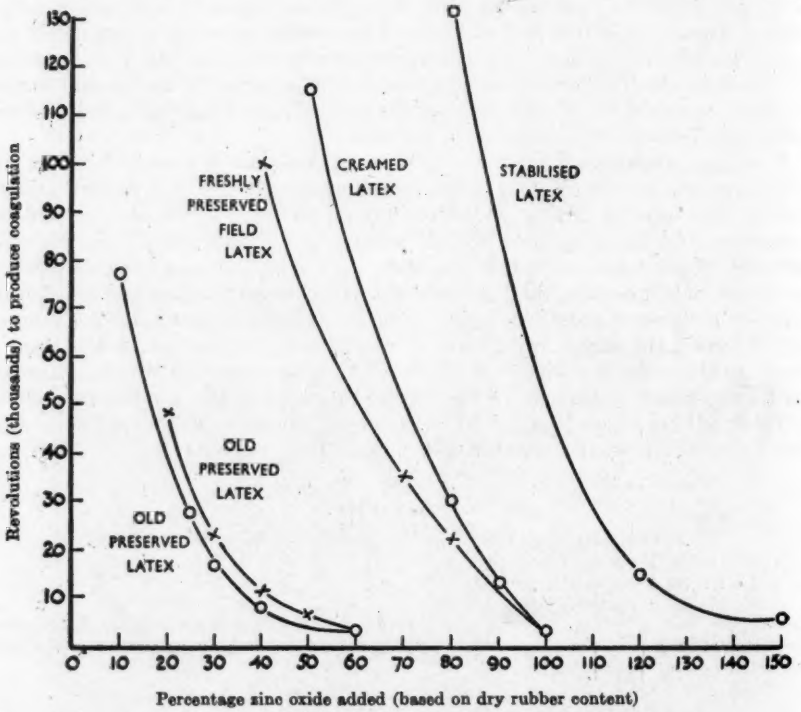


Figure 7—Stability Test on Different Latices

The effect of varying the ammonia content is shown in Fig. 8, all the other factors being standardized. Two types of zinc oxide were used, White Seal and colloidal. Within the range of alkalinity such as is likely to occur in commercial latex, the effect of ammonia is not so marked as with higher amounts. With White Seal zinc oxide, coagulation occurs relatively quickly with a latex of low ammonia content, the period being gradually increased as the ammonia content of the latex increases. On the other hand the period required to produce coagulation of the latex in the presence of colloidal zinc oxide is less affected by variations in ammonia content, particularly with concentrations of 0.5 to 3 per cent. Owing to the fine state of subdivision of the colloidal zinc oxide the material disperses more easily than White Seal zinc oxide, and coagulation therefore does not occur so readily. In the presence of larger amounts of ammonia, White Seal zinc oxide particles are prevented

from causing relatively quick coagulation by the larger negative charge on the rubber particles, and the consequent lower viscosity of the latex.

In order to determine the relative effects of temperature, a series of determinations of stability was made at different temperatures, ranging from 37° to 110° F. The results in Fig. 9 show that the effects of temperature on stability are more pronounced than those produced by a varying ammonia content of the latex; stability increases rapidly at temperatures below normal room temperature. This appears to be of considerable practical interest, and also emphasizes the importance of constant temperature conditions in carrying out this type of stability test.

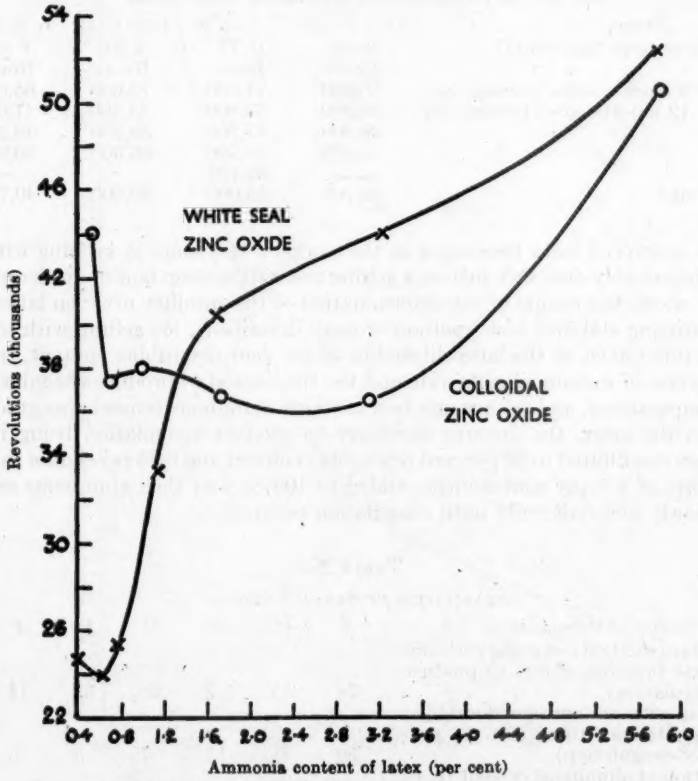


Figure 8—Effect of Ammonia Content on the Stability of Latex

The method used in routine testing is as follows: the latex is adjusted to a dry rubber content of 30 per cent, and an alkalinity of 0.6 per cent ammonia or its equivalent. Fifty cc. of this latex, to which 50 per cent of White Seal zinc oxide based on the dry rubber content (or a higher percentage if the latex is particularly stable) is quickly added, is stirred at a speed of 2000 revolutions per minute, and the number of revolutions necessary to cause coagulation noted. The temperature of the water circulating in the jacket is maintained at 30° C.

Reference was made in an earlier section of the paper to a series of latices preserved with different amounts of ammonia in order to observe the effect on the keeping properties. The stabilities of these latices were determined 6 and 12

months after preparation. For comparative purposes the ammoniacal content of each latex was raised to that of the latex with the highest content. The results are shown in Table IX, the individual results being given in order to demonstrate the reproducibility of the method. They are also of interest in showing that the quantity of ammonia used in practice is around the optimum with respect to its effect on stability. There is no object to using larger amounts as this evidently hydrolyzes the proteins protecting the rubber globules and accelerates the fall in stability.

TABLE IX

EFFECT OF STORAGE ON THE STABILITY OF LATEX

Sample	L. A. C. 15	L. A. C. 16	L. A. C. 17	L. A. C. 18
Ammonia content (per cent)	0.56	0.77	1.24	1.62
	Revs.	Revs.	Revs.	Revs.
Stability 6 months after preparation	56,000	71,000	73,000	65,000
Stability 12 months after preparation	46,600	53,800	43,400	41,000
	39,700	47,700	39,200	40,200
	44,400	53,300	36,300	40,900
	—	56,100	—	—
Average	42,700	53,000	39,600	40,700

In the control of latex processing in the works, a test more in keeping with the process is probably desirable such as a gelling test with a coagulant or an electrolyte. Table *X* shows the results of the determination of the stability of seven latices, by (*a*) the stirring stability test (method already described), (*b*) gelling with sodium silicofluoride (50 cc. of the latex diluted to 40 per cent dry rubber content, treated with 2 grams of sodium silicofluoride and the time noted to produce coagulation at room temperature), and (*c*) a rough test in which aluminous cement was gradually added to the latex, the amount necessary to produce coagulation being noted. (The latex was diluted to 30 per cent dry rubber content and 0.75 per cent of saponin in the form of a 5-per cent solution added to 100 cc. and then aluminous cement added slowly and uniformly until coagulation occurred.)

TABLE X

STABILITIES OF SEVEN LATICES

	Method of Determination	A	B	C	D	E	F	G
1	Standard method—stirring with zinc oxide (number of rev. to produce coagulation)	74	55	53	26	33	14	5
2	Gelling with sodium silicofluoride at room temperature (min. to produce coagulation)	50	45	15	7	5	5	8
3	Addition of aluminous cement (g. of cement added to produce coagulation)	400	400	400	400	345	280	338

ORDER OF STABILITY

	A	B	C	D	E	F	G
Method 1	1	2	3	5	4	6	7
Method 2	1	2	3	5	6	6	4
Method 3	1	1	1	1	5	7	6
	Equal						

There is not an exact correlation in the results, which could hardly be expected, as one test is chiefly a mechanical test, the second a chemical test, and the third

partly physical and partly chemical. There is, however, a general classification, A, B, and C being superior to other latices in all these tests.

Film Strength.—Suggestions have been made that the tensile strength of the dried latex film should be utilized as a criterion of quality for certain purposes. The preparation of latex films to a certain stage is a simple matter, and several methods have been proposed for this purpose: (1) drying the latex on smooth

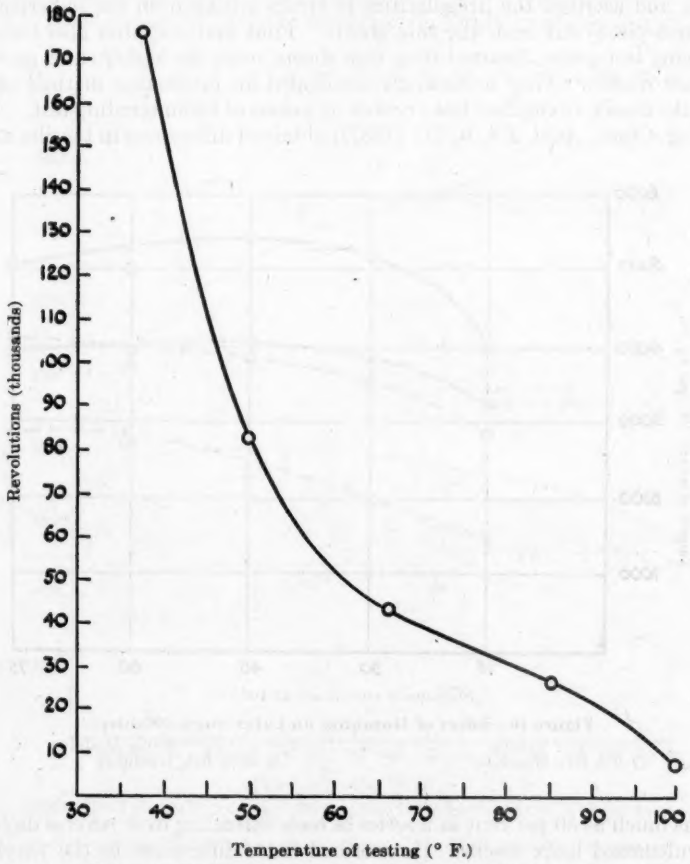


Figure 9—Effect of Temperature on the Stability of Latex

surfaces, such as stainless steel or glass in air at room temperatures or at 45° C. (*du Pont Laboratory Report*, No. 181, **1934**); (2) drying the test films at room temperature on unglazed tiles bounded by strips of paper treated with paraffin wax (*Vanderbilt News*, Sept.-Oct., **1934**); (3) drying the latex on mercury in a tin frame, with which the mercury amalgamates, and so reduces both the tendency of the dried film to adhere to the frame and the possibility of cracking. A film of 1 mm. is a convenient thickness, as it compromises between a reasonable period of drying, for example, at 30° C., and a measurable breaking load on the tensile machine. After approximately 24 hours' air drying the film is in a suitable condition to enable

it to be removed from the drying mold; but the last traces of moisture are difficult to remove, and it is this final stage of drying, depending upon its nature and extent, which appears to be responsible for the varying results noted by different workers.

Flint and Naunton (*Trans. Inst. Rubber Ind.*, **12**, 367 (1937)) encountered difficulties when attempts were made to determine the tensile strength of thin sheets (0.2–0.4 mm.) by standard methods. They found that the determinations were not reproducible within any acceptable margin of error, particularly in undervulcanized samples, and ascribed the irregularities to errors arising from the imperfect edges of the test-pieces cut from the thin sheets. Flint and Naunton also found that when using test-pieces stamped from thin sheets, even the higher cures gave hopelessly low results. They accordingly developed an interesting method of determining the tensile strength of latex rubber by means of a film bursting test. Wohler (*Ind. Eng. Chem., Anal. Ed.*, **9**, 117 (1937)) obtained differences in tensiles amount-

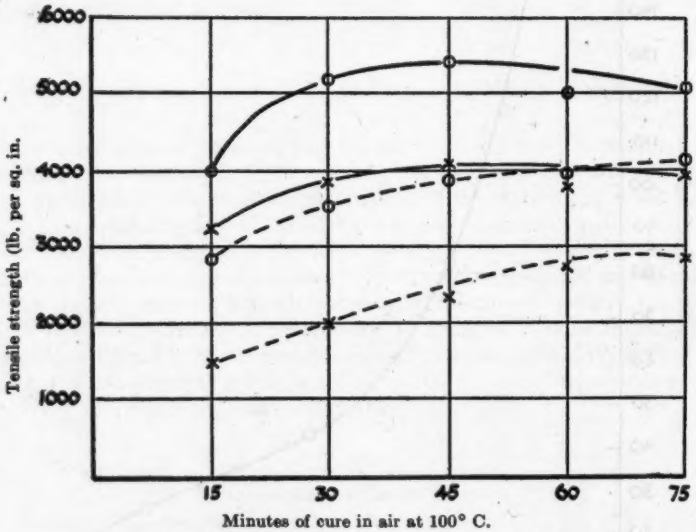


Figure 10—Effect of Humidity on Latex Stock (Wohler)

——— Tensile — — — — 800% Modulus
○ 0% Rel. Humidity × 50% Rel. Humidity

ing to as much as 50 per cent in a series of tests extending over several days on the same vulcanized latex stocks. He ascribed these differences to the varying humidity conditions prevailing at the times of the tests, and showed that the modulus and tensile strength of the test-pieces conditioned for 48 hours at 50 per cent relative humidity were 30 per cent less than those of the ones conditioned in a day atmosphere (Fig. 10). A series of repeat tests on similar samples conditioned for 48 hours at 0 per cent humidity gave identical results.

Effects similar to those noted by Wohler with vulcanized latex films have been observed with unvulcanized latex films. The removal of the last traces of moisture by means of a dehydrating agent produces a marked increase in modulus and tensile strength, which continues to increase long after the rubber reaches a constant weight. Similar results are obtained when the latex film is dried *in vacuo*. Drying at an elevated temperature produces a hardening in the early stages, which is after-

wards balanced by the softening due to the heating, giving a period throughout which the tensile strength remains fairly constant.

Similar phenomena have been observed in plasticity determinations of estate sheet and crepe, a marked hardening in the early stages of heating being followed by the softening due to oxidation.

Figure 11 shows the results of modulus and tensile strength determinations on raw latex rubber films dried respectively over sulfuric acid *in vacuo* and at 70° C. The raw rubber films stored over sulfuric acid were still increasing in strength after 34 days. This increase can only be explained by assuming that a change in state

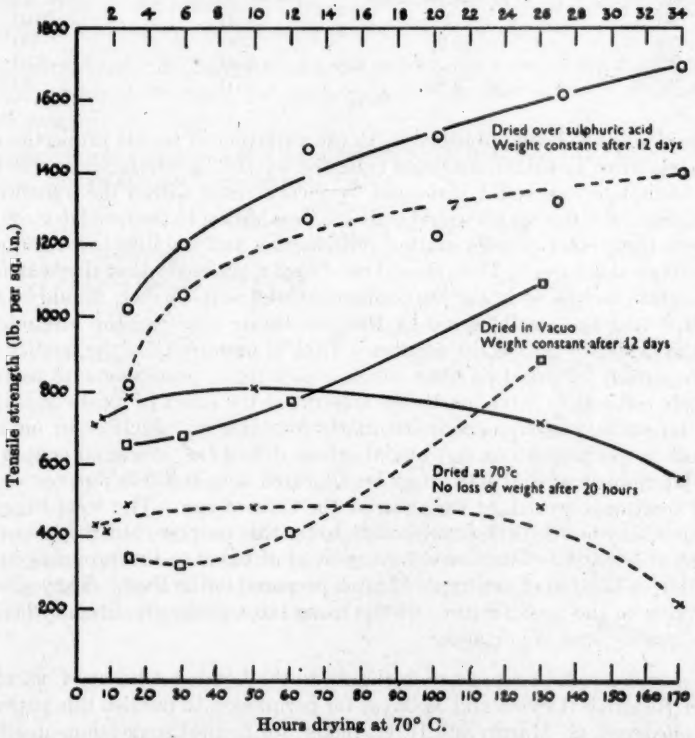


Figure 11—Tensile Strength of Films from Concentrated Latex at Varying Stages of Drying

——— Tensile strength at break — — — — Load at 900% elongation

akin to polymerization is taking place in the dry rubber. The rubber dried *in vacuo* follows a similar course, but the change is more gradual. The rubber dried in the oven at an elevated temperature reaches approximately only one-half the strength attained by the rubber dried by means of the dehydrating agent.

Raw rubber films also are more susceptible to the temperature of testing and the rate of stretching than the corresponding vulcanized films.

By carefully standardizing the conditions of testing, the tensile test is of value in identifying latex which has depreciated through being shipped in dirty drums or latex which has been treated to conform to market requirements as to color. The occurrence of such latices could be identified more easily by a method suggested by

Murphy (privately communicated), which consists in aging the raw rubber film for 16 hours at 95–100° C., after which treatment normal latex rubber still retains its strength. This method obviates the determination of the initial tensile strength. Table XI shows the respective tensile strength and aging results for two standard latices treated with hydrogen peroxide in order to restore their color.

TABLE XI

EFFECT OF HYDROGEN PEROXIDE ON AGING PROPERTIES OF DRIED LATEX FILMS

Sample No.	Amount of Hydrogen Peroxide (20 Vols. Solution)	Tensile Strength before Aging	Tensile Strength after Aging
30/3	...	680	610
30/3	1%	190	30
22/5	...	650	640
22/5	1%	170	80

No evidence has been published as to the variation in tensile properties of films from fresh latex, but data are being collected by the Research Scheme in Ceylon.

The tests described could, if desired, be incorporated within the framework of a specification for latex, which would embrace, in addition to the usual dry rubber and alkalinity tests, color, foreign matter, putrefaction and stability tests, and possibly a dry rubber aging test. They should be of such a character that they can be made on the estate as well as in the importing countries and, further, should be capable of interpreting the results given by the best estate practice, the ultimate object being the raising of the quality of latex. Lack of uniformity in the quality of latex is an important technical problem which is sometimes troublesome to users and is extremely difficult to solve, partly on account of the effect of local conditions and partly on account of changes (particularly in stability) which occur on keeping. Although a specification cannot obviate these difficulties, it should enable quality to be determined so that latex may be allocated to a suitable purpose or receive special treatment to reduce variation at the time of use. The tests suggested in this paper may not be sufficiently complete for this purpose, but they represent an attempt at scientific control, and have proved of value to the producer in the examination in London of new types of latex prepared in the East. They should also be of value to the manufacturer who is using latex under conditions where variation in quality is of importance.

The authors wish to express their thanks to the London Advisory Committee for Rubber Research (Ceylon and Malaya) for permission to publish this paper and to their colleagues, G. Martin and H. C. Baker, for helpful suggestions made during the preparation of the paper.

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Some Properties of Rubber Latex

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Rubber latex of the commercial type preserved by ammonia was freed almost completely of its serum components by a method involving two steps:

1. Electrophoretic deposition of the rubber particles on a membrane, followed by
2. Dispersion of the resultant paste in a 0.6-per cent solution of ammonia in distilled water.

This process was repeated until the aqueous phase obtained from this separation was free of non-rubber components in the latex.

TABLE I

Concentration Percentage by Weight of Dry Residue	Density
0	0.9965
0.25	0.9961
2.73	0.9940
3.58	0.9928
19.70	0.9784
28.70	0.9697
32.50	0.9666
37.80	0.9615
53.70	0.9469

The relation between the density of this dispersion of rubber (the dispersed phase of which contained only traces of serum, probably adsorbed on the surface of the rubber particles) and its degree of dilution was then determined. The curve obtained was then extrapolated to zero dilution.

TABLE II

η/η_0	V/V_0	η/η_0	V/V_0
27.7	1.618	38.84	1.59
27.8	1.573	20.84	1.26
23.4	1.52	19.24	1.24
23.4	1.517	17.68	1.17
5.78	0.755	16.93	1.17
3.61	0.530	13.63	1.068
2.99	0.44	7.595	0.789
2.64	0.407	6.08	0.685
1.95	0.261	3.73	0.451
1.48	0.172	2.80	0.334
		2.37	0.234
		1.42	0.214
		1.05	0.018
		1.016	0.0047
		1.00	0

It was found by extrapolation in this way that the density of rubber is 0.905 at 18° C. (see Table I and Fig. 1). In Fig. 1 the abscissa represents the concentration

and the ordinate, the density of the dispersion. The density of the rubber obtained after drying was 0.909. The determinations were made at approximately 18° C.

In subsequent experiments the relation between concentration and viscosity was studied. The viscosity determinations were made with a Höppler viscometer. In all cases the rubber paste was diluted with the aqueous phase obtained by the separation. The results of these determinations are shown in Fig. 2, and are compared with an unpurified rubber latex. Here the abscissa represents the relation

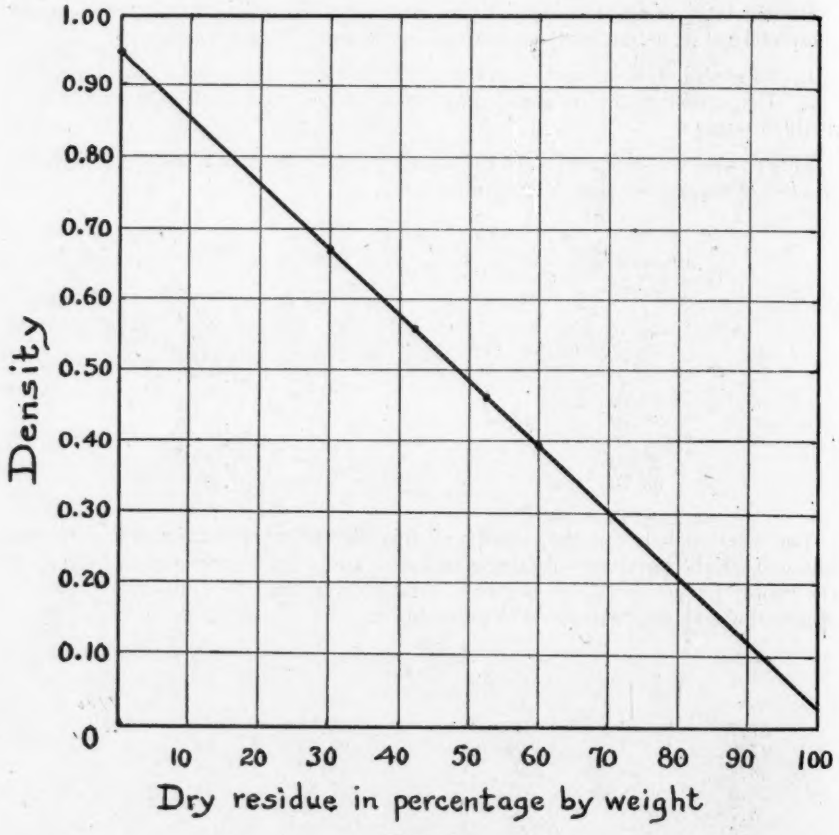

Figure 1

between the volume V of the dispersed phase and the volume V_0 of the dispersion liquid. The ordinate represents the relation between the viscosity η of the dispersion and the viscosity η_0 of the dispersion liquid (serum).

As is evident in Fig. 2, the viscosity of the purified product is much lower than that of the original latex. This change can be explained by the suggestion offered by Blow (cf. *Trans. Faraday Soc.*, **25**, 458 (1929)), who is of the opinion that the adsorbed and solubilized layer on the rubber particles dissolves when the system is diluted with the aqueous phase. As a result of this dilution, the volume of the dispersed phase diminishes in relation to that of the aqueous phase. At higher

concentrations this difference in the viscosities is considerably greater because the relation between viscosity and concentration is exponential rather than linear.

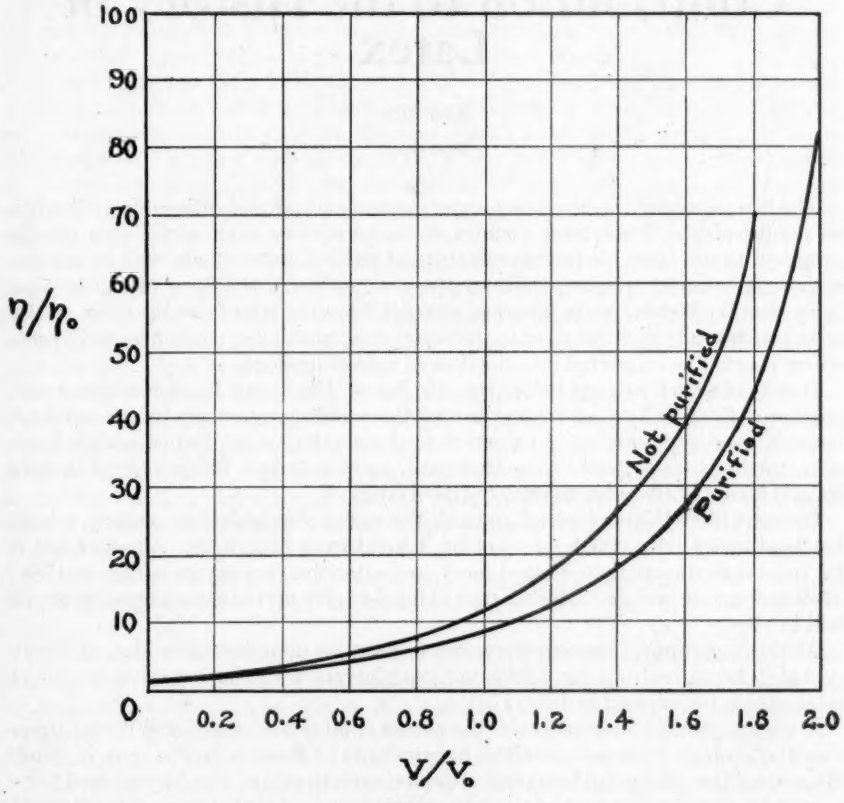

Figure 2

The thickness of this adsorbed layer could not be calculated because none of the formulas derived for calculating the volume of the disperse phase from the viscosity was found to be sufficiently exact.

[Translated for Rubber Chemistry and Technology from the Recueil des Communications du Congrès International du Caoutchouc, Paris, pages 7–8, June, 1937.]

Contribution to the History of Latex

Leo Eck

DORTMUND

The first move towards the direct use of latex was by Arnold Juliaans in 1780 when he published his "Dissertatio chemica de resina elastica cajennensi." In this he proposed to use latex for the manufacture of medical instruments such as sounds, catheters, bougies, syringes, milk pumps, etc., either in the form of the original juice from the Hevea tree in America, where it flowed as latex from the trees, or else after transportation of this latex in the liquid state in suitable containers to Europe, where it could be converted into the desired rubber products.

It is true that ten years before this Sir Joseph Banks, an English explorer and partner of Cook in his first voyage around the world, had brought back a bottle of latex in good condition, as a narrative by Grossart shows. Unfortunately however, the latex decomposed soon afterward, and Sir Joseph Banks offered in vain 50 gold louis at Lisbon for another bottle of latex.

Grossart himself had received, towards the end of the eighteenth century, a half-bottle of milky juice which was sent by d'Arcet from Mauritius. Grossart left it for several winters in an unheated room, and after the very severe winter of 1788–1789 he found it broken. He was thus obliged to give up the experiments which he had in view.

At this same time, Fourcroy appeared to have hit upon the same idea, and very probably he carried out his celebrated experiments with the second shipment of latex, which he received in July, 1791.

A very important observation on the nature of latex was made by Wilhelm Heinrich Buchholz in 1799, as a result of his attempts to dissolve elastic resin in ether. He noticed that an insoluble deposit appeared each time, and this he supposed to be a "residue of the milky part of the juice of this tree." One is tempted to interpret this as a description of proteins insoluble in ordinary rubber solvents, which according to present knowledge accompany the rubber particles. As a matter of fact Juliaans, already mentioned above, was the first to find a nitrogen compound (ammonia) in the distillation products of rubber.

The contributions of Fourcroy to the chemistry of latex are for the most part already known. However, as a result of detailed studies of the early history of rubber, certain points which have been previously overlooked may be mentioned. Fourcroy examined three shipments of latex from Réunion, Cayenne, and Brazil (1785–1791). In each case he observed the same phenomenon of the formation of an elastic substance. It is improbable that the shipment of latex from Réunion was Hevea latex.

According to the records of Fourcroy, he found in the bottles, besides a white turbid liquid of insufferable odor, a solid, white, somewhat spongy mass of true rubber. It may be concluded that he no longer had undecomposed latex at his disposal. The liquid portion of his latex samples contained only one-thirtieth of the original content of rubber in the latex. This explains why he recommended the addition of alkali to latex at the beginning. This he tried himself in an at-

tempt to preserve his latex. He also advised marking on the bottles the time of tapping, quantity, quality, specific gravity, taste, and odor before adding any alkali.

It should be mentioned that Fourcroy believed that absorption of oxygen was the cause of separation of rubber from the latex, and he supposed that the coagulation of rubber is always closely related to an oxidation process.

He also described the precipitation of rubber by alcohol, and he was well aware of the fact that an elastic substance is precipitated by addition of hydrochloric acid. However, according to him the solid elastic product was formed only when the latex was in contact with air or rather when "the oxidized hydrochloric acid" or "oxygenated muriatic acid" reacted with it. Presumably oxygenated muriatic acid was none other than chlorine, which was employed probably in the form of chlorine water.

In his essay "on the juice which yields elastic gum," which appeared in 1791, Fourcroy describes observations which he made when he opened the bottles. According to him there was a powerful, unbearable odor of hydrogen sulfide and of rotted garlic. It has already been mentioned that this is the first proof that sulfur is an element which is normally present in rubber latex.

Fourcroy has contributed further to the chemistry of latex by his investigations of crystals obtained by evaporation of serum. These crystals, which were grouped in radial form, were yellow, had a slightly acidulous, sugary taste, and were soluble in water and in alcohol, with an acid reaction to litmus. They gave no precipitates in solutions of silver nitrate and mercury nitrate, as was also the case with lime water. From this Fourcroy concluded that these crystals might be formed of a "sugary substance" which had commenced to change into an acid. In view of the uncertainties involved in the analysis of organic substances in the days of Fourcroy, it is remarkable that the presence of sugar in latex should be confirmed at a later time.

The publications of Fourcroy gave an impetus to a whole range of investigations of the milky juice, the results of which were published around the beginning of the nineteenth century. There might, for instance, be mentioned the "Recherches comparatives de suc laiteux indigènes au suc laiteux du caoutchouc" by Carradori, the "Essais sur un produit de la Castilloja elastica" by Fourcroy and Vauquelin, and the "Recherches du suc de papaya" by Cadet-Gassicourt, on the one hand, and by Vauquelin, on the other. Numerous others might likewise be cited. The first two are unquestionably the most interesting ones, and for this reason it would seem well to dwell on them for a moment.

In the first place, it is of interest to note the growing knowledge of colloidal phenomena which is evident in so striking a manner in these works. Whereas Fourcroy supposed that rubber was actually dissolved in the milky juice, Corradori came close to the truth when he assumed that "the resinous component which coagulates is either dissolved or floats in an aqueous liquid." He was also familiar with the effect of alkalies in preventing precipitation.

Vicente Cervantes, a professor of botany in Mexico, who is mentioned in the work of Carradori, but about whom no further details could be found, attributed the blackening of a rubber separated from the milky juice of *jatropha* to the influence of air and also to the influence of sunlight, for under water the rubber remained white. In addition to this, Cervantes pointed out the resemblance of the milky juice to a plant emulsion.

The interest shown in the problem of latex by scientists of that time is also evident in the fact that "our distinguished compatriot traveler," called thus by the German chemist Gehlen-Alexander von Humboldt, sent to Paris, at the request of Fourcroy,

latex from various plants for his researches. A bottle of latex from the *Castilloja elastica*, brought back from a voyage to Mexico in 1804, was analyzed by Fourcroy and Vauquelin. Since in this case also the latex had already decomposed when received, it again came chiefly to a question of analyzing the serum. An examination of the separated rubber led the two scientists to the following observations.

When the coagulum was placed on a plate, the particles gradually contracted as if they were pulled together by a force originating in their center, and a red-brown liquid was squeezed out in abundant quantity. This may very well be the first description of the syneresis of rubber particles. The serum had an acid reaction, and it contained, among other substances, potassium chloride and potassium acetate. It must be remembered, however, that for lack of any other term at that time, various organic acids were designated as "acetic acid." The authors believed that the function of the potassium in the latex of *Castilloja* could be explained by assuming that originally it is united to the rubber and maintains the latter in a state of suspension. The acid which is formed by fermentation of the milky juice is set free from the rubber and then fixes the alkali present; as a result the rubber separates. This supposition would, however, require confirmation by the behavior of fresh milky juice. Then again, it is not applicable to all juices containing rubber, for some of these various juices do not contain any alkali.

There are numerous other observations and theories in the early literature of rubber which, in spite of a certain lack of knowledge at the time, are well worth being more widely known and also made available in published form.

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Sorption of Water by Rubber

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THE presence of water is one of the principal causes of electrical instability in dielectric materials, often resulting in large variations in direct current resistance, dielectric constant, and power factor. A knowledge of the laws governing the sorption of water is therefore of considerable interest to the electrical and communications industries.

The various investigators in the field of sorption of water by rubber have not reported their findings in a manner which will permit of consistent interpretation and correlation for engineering uses. Insufficient attention has been given to the effect of such factors as shape of test specimen, temperature control, variations in vapor pressure, chemical changes in the test specimen, etc. Consequently no sorption coefficient suitable for application to practical problems and no measure of the rate of sorption which will permit an adequate comparison of one material with another is now available.

The purpose of this article is to describe the relation between rate of sorption and some of these variables, such as thickness of test specimen, temperature, and vapor pressure, and to show how sorption tests can be applied to certain practical problems. It is not the purpose to present a survey of the literature. The word "sorption" is used in conformity with current phraseology to mean the combined effect of adsorption and absorption.

Variation of Rate of Sorption with Time

The most important factor governing the sorption of water by an insulating material is the vapor pressure with which it is in contact. When, at some fixed relative vapor pressure and temperature, thin sheets of a material such as rubber are immersed in water or water vapor, they sorb water at a rate described by the curves in Figure 1. In this figure the increase in weight, c, in per cent is plotted against time of immersion in days. c, then, represents the grams of sorbed water per 100 grams of dry material. These curves are obviously parabolic and suggest that, if the logarithm of the increase in weight is plotted against the logarithm of time, a straight line will be obtained, which is usual with this type of sorption isotherm. Figure 2 shows the data from Figure 1 replotted on logarithmic paper. The curves of the four different thicknesses are nearly parallel straight lines. Since

the thin sheets sorb water at a faster rate than the thick, the curves shift upward on the graph with decreasing thickness.

The straight-line equation describing these curves is:

$$\ln c = n(\ln t - \ln t_1) + \ln c_1 \qquad (1)$$

or

$$c = c_1 \left(\frac{t}{t_1}\right)^n \qquad (2)$$

where c = increase in weight in per cent, or the per cent sorbed water at time t

c_1 = experimentally determined water at time t_1

n = slope of increase in weight-time curve in Figure 2

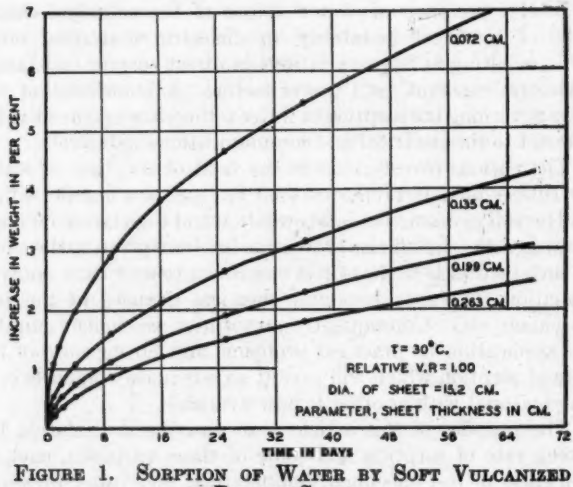


FIGURE 1. SORPTION OF WATER BY SOFT VULCANIZED RUBBER SHEETS

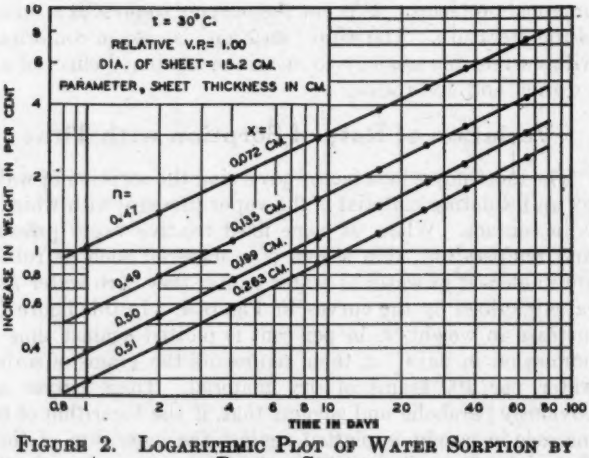


FIGURE 2. LOGARITHMIC PLOT OF WATER SORPTION BY RUBBER SHEETS

Slope n is apparently independent of thickness or shape of test specimen; and as long as the test specimen, the tempera-

ture, and the relative vapor pressure remain constant, n will not vary. For a relative vapor pressure of 1.00 (100 per cent relative humidity) n has the value 0.50. Equation 2 consequently reduces to an easily remembered relation,

$$c = c_1\sqrt{t} \qquad (3)$$

where c_1 = measured increase in weight at some unit time, such as 1 day or 1 week

It thus becomes possible to calculate from short-time test data the water content of a sorbing material such as rubber after any period of exposure to 100 per cent relative humidity. A rubber specimen which, for example, sorbs 0.1 per cent water in one day will sorb ($c = 0.1\sqrt{3650}$) or 6.0 per cent water after 10 years under fixed conditions of exposure.

Equation 3 indicates that, if the increase in weight, c, is plotted against the square root of time, a straight line will be obtained whose slope, $c/\sqrt{t}$, is equal to c_1, the increase in weight at unit time t_1. This relation is illustrated in Figure 3. Each thickness has a different slope, the greater slope indicating a higher rate of sorption. In Figure 3 the rate of sorption is expressed by the slope of the curves, but in Figure 2 the rate is indicated by a shifting of the curves along the ordinate.

After the studies described in this paper had been completed, the attention of the authors was called to an excellent article on the sorption of water by rubber, published in Japanese by Satake (*6*); he plotted the logarithm of the water content against the logarithm of time in a manner similar to Figure 2 of the present paper. Satake pointed out that during the initial period of immersion the sorption of water by vulcanized rubber was directly proportional to the area exposed and varied as the square root of time. He suggested that during the later stages the process conformed more nearly with an equation derived by Andrews and Johnston (*1*). Several experimenters have, however, presented data which indicate that in the case of rubber the parabolic curve for increase in weight *vs.* time is valid over long periods of time, particularly if the rubber does not offer excessive resistance to swelling at the higher water contents. Lowry and Kohman (*4*), for instance, carried their sorption tests over a period of 440 days. Their data for three compounds are plotted in Figure 4. Kemp (*3*) presented data on pale crepe and smoked sheet immersed in distilled water which followed the same relation over a period of 1100 days. Soule (*7*) gave data on various fillers which sorbed water as the square root of time over a period of 42 days. Data of Messenger and Scott (*5*) show that the square root relation holds for rubber rings, and unpublished data of the authors indicate that the relation holds for rubber-covered wire. In their explanation of the time lag in diffusion, Wosnessensky and Dubnikow (*9*) present a sorption equation in which the mass of water sorbed is

proportional to the membrane area and to the square root of time.

Several factors will cause the curve for increase in weight *vs.* time to deviate from the shape of a parabola. Some of these factors may account for the many discrepancies in the literature. One of the most common is temperature variation during the test. At room temperatures, for example, a variation of 1° C. effects a 6 per cent change in vapor pressure. A more serious factor is lowering of the relative vapor pressure due to contamination of the water by a leaching out of water-soluble materials. Data presented by Lowry and Kohman (*4*) show that a decrease of 1 per cent in relative vapor pressure from 1.00 to 0.99 will lower the rate of sorption as much as 50 per cent. It is therefore essential in carrying out sorption tests where the sample is immersed that the water be changed often enough to prevent contamination. The leaching of water-soluble material by the test specimen will tend not only to decrease the slope of the $\ln c$ *vs.* $\ln t$ curve by contaminating the water, but also by decreasing the water sorbing impurities within the test piece. The effect is believed to be accentuated by the fact that much of the sorbed water is concentrated in the outer layers of the material. The loss of water-soluble material may be largely eliminated by carrying out the test in water vapor instead of in water. The change in rate of sorption resulting from the removal of water-soluble impurities may be seen by comparing curves *B* and *C* in Figure 4. Curve *B* is shifted downward and becomes curve *C* when rewashed smoked sheet is used in place of commercial smoked sheet. In Figure 2 the smaller slope of the thinner sheets and the decrease in the rate of sorption of all the sheets after the test had progressed for about 40 days is attributed to leaching of some water-soluble material from the rubber.

Since the result of natural or added impurities is to shift the increase in weight *vs.* time curve upward, the formation of oxidation products will also be evidenced by an increased rate of sorption. The effect of this type of deterioration is illustrated by the increased slope of curve *B* in Figure 4 after about 150 days of immersion. The true value of n apparently remains unchanged, but, since deterioration increases exponentially with time, the curve is progressively shifted upward as suggested by the broken lines in Figure 4. If the oxidation process could be halted, the sorption of water would be resumed at a higher rate and with a slope of 0.50. The effect would be similar to that obtained by the addition of a fixed amount of water-soluble impurities at some time during the sorption process or to aging in the Geer oven for a time. An increase in the slope of the curve for $\ln c$ *vs.* $\ln t$ may accordingly be used to detect progressive aging, and the increased slope of the curve for c *vs.* $\sqrt{t}$ may be used as a quantitative measure of the formation of deterioration products.

Another factor influencing the rate of sorption is hardness of the material. In Figure 4 the compound containing 5 per cent sulfur (curve *A*) takes up water at a greater rate than

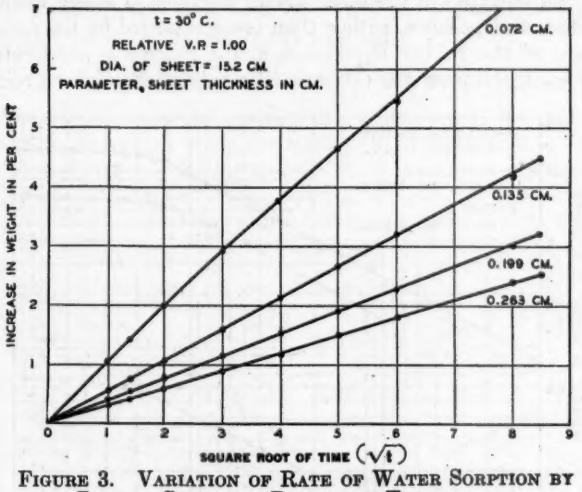


FIGURE 3. VARIATION OF RATE OF WATER SORPTION BY RUBBER SHEETS OF DIFFERENT THICKNESSES

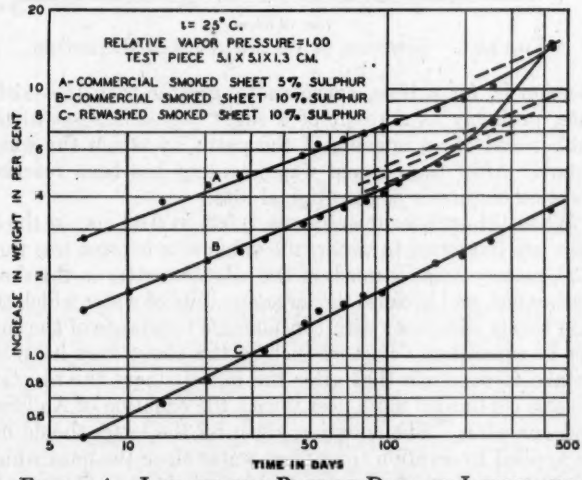


FIGURE 4. LOGARITHMIC PLOT OF DATA OF LOWRY AND KOHMAN FOR SORPTION OF WATER BY RUBBER SHEETS

the harder compound containing 10 per cent sulfur shown by curve *B*. The effect of increased hardness is to shift the entire curve downward on the graph toward lower values of gain in weight. Should the sorption test be made at a temperature sufficiently high to cause additional vulcanization, a progressive decrease in the slope of the ln c *vs.* ln t curve below $n = 0.50$ would occur.

When rubber sheets are immersed for a time in distilled water and dried, the rubber loses water much more rapidly than it gained water. This occurs because much of the water is concentrated in the outer layers where it is easily evaporated, and because, rather than being retarded by the resistance of the rubber to expansion, the process is accelerated by contraction of the rubber. The rate of sorption on reim-

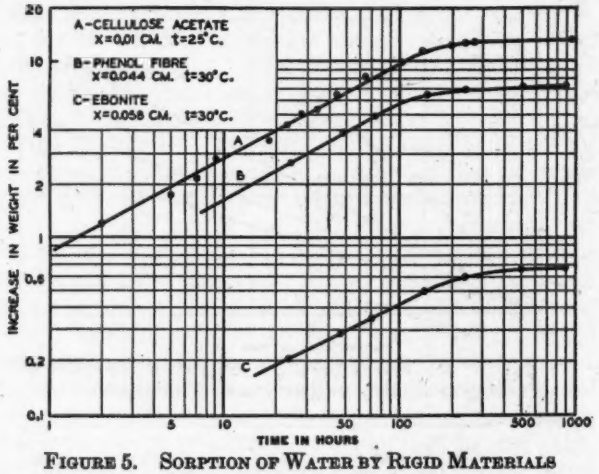


FIGURE 5. SORPTION OF WATER BY RIGID MATERIALS

mersion is, for a time, considerably greater than the initial rate, probably as a result of a slight permanent set in the rubber and of an opening of the paths by which the water enters. After the original water content has been reached, sorption continues at the original rate.

When thin rubber membranes, 0.005 to 0.03 cm. in thickness, are immersed in water, the value of n is often less than 0.50, mainly because much of the soluble matter in the sheet washes out, and because the large amounts of water which the thin sheets sorb meet with considerable resistance of the rubber to expansion. Factors such as the above may have led Satake to conclude that after the initial stages the sorption process conformed more nearly with the equation of Andrews and Johnston. The equation given by the latter should not be applied to sorption from fresh water since the data which they gave and which the equation was derived to fit were obtained in 3.5 per cent salt solution at a room temperature which varied considerably.

The lower rate of sorption of high-modulus rubber compositions, due to their resistance to swelling, suggests that with rigid materials n will drop to zero when the resistance to swelling by the material is sufficient to make the vapor pressure of the sorbed water equal to that of the solution on the outside. The fact that one rigid material takes up less water than another does not necessarily mean that it contains less

water-soluble material, for it may be more rigid. Sorption curves of three rigid materials are given in Figure 5. The data on cellulose acetate are a replot of those published by Wosnessensky and Dubnikow (*9*). The data for ebonite and phenol fiber were obtained by the authors.

Effect of Vapor Pressure

Sorption of water by a material is a function of the vapor pressure in contact with the surface of the material. The sorption process will be complete when the vapor pressures external and internal to the material are equal. When the logarithm of the sorbed water is plotted against the logarithm

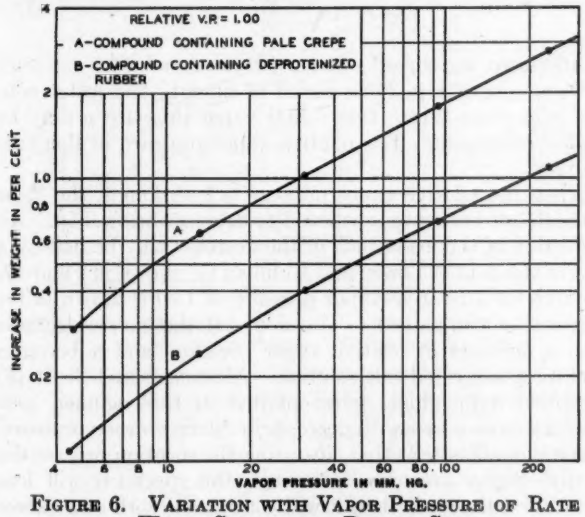


FIGURE 6. VARIATION WITH VAPOR PRESSURE OF RATE OF WATER SORPTION BY RUBBER SHEETS

(Data taken after 3-day immersion in water.)

of vapor pressure, a straight line results. Figure 6 is a logarithmic plot of the per cent increase in weight of rubber sheets against the corresponding vapor pressure. The relative vapor pressure is 1.00 throughout. These data were obtained by measuring the increase in weight, c, after 3-day immersion in distilled water at various temperatures. The curve is not quite straight, particularly in the lower temperature region. Furthermore, the slope in this region is slightly greater than 0.50. Such a variation is common in those materials which undergo changes in hardness or in dimensions with temperature changes. An increase or decrease in the solubility of the water-soluble impurities with change in temperature will also alter the slope of the curve.

Neglecting variations in the material, the straight-line equation expressing the relation between increase in weight and vapor pressure is

$$\ln c_2 = n_1 (\ln p - \ln p_1) + \ln c_1 \qquad (4)$$

where c_2 is the increase in weight at some vapor pressure, p, and n_1 and c_1 are experimentally determined at pressure p_1. This equation may be combined with Equation 1 by substituting ln c_2 from Equation 4 for ln c_1 in Equation 1 to give the more general equation:

$$\ln c = n \ln \frac{t}{t_1} + n_1 \ln \frac{p}{p_1} + \ln c_1 \qquad (5)$$

or

$$c = c_1 \left(\frac{t}{t_1}\right)^n \left(\frac{p}{p_1}\right)^{n_1} \qquad (6)$$

If n and n_1 are both taken as 0.50, Equation 6 becomes:

$$c = c_1 \sqrt{\frac{t}{t_1} \frac{p}{p_1}} \qquad (7)$$

If, therefore, the sorbed water, c_1, is measured after exposure to vapor pressure p_1 for a period of time, t_1, the water content c at some future time t and vapor pressure p may be readily calculated. The relative vapor pressure in this case is unity.

When the relative vapor pressure is less than 1, the slope of the ln c *vs.* ln t curve is believed to decrease below 0.50. An indication of the magnitude of the decrease may be had by a plot of the data of Lowry and Kohman (*4*) shown in Figure 7. A curve for a relative vapor pressure of 1.00 is drawn in for purposes of comparison. The slopes of the curves decrease with a decrease in relative vapor pressure, and n becomes 0.09 for a saturated salt solution. Messenger and Scott (*5*) presented data which, when plotted in this manner, also show a decrease in n with decrease in relative vapor pressure. These data illustrate that, if during the sorption process the relative vapor pressure is lowered, the specimen will lose water for a time and then it will continue to sorb at a slower rate until equilibrium at this new relative vapor pressure is reached. The above data are not in agreement with those of Satake (*6*) who found n to be 0.50 for sorption in various salt solutions. Satake stopped his tests on rubber after 42 hours. The present authors' experience indicates that the slope n at a relative vapor pressure of 0.98 was nearly the same as the slope in distilled water—namely, 0.50—during the first 3 days of the test, after which it assumed a lower and constant value. Differences in test time may possibly explain the lack of agreement. The available data do not permit of definite conclusions, and additional experimental work will be necessary to clarify the effect accompanying lowering of the relative vapor pressure.

Effect of Temperature

The major effect of a change in temperature is an alteration of the vapor pressure. Since at ordinary temperatures the logarithm of the vapor pressure of most liquids is a linear function of the reciprocal of the absolute temperature, it

follows from the ln c *vs.* ln p relation that ln c will vary linearly with $1/T$. Figure 8 shows this to be the case. The relation between increase in weight and absolute temperature is:

$$\ln c_3 = m\left(\frac{1}{T_1} - \frac{1}{T_3}\right) + \ln c_1 \qquad (8)$$

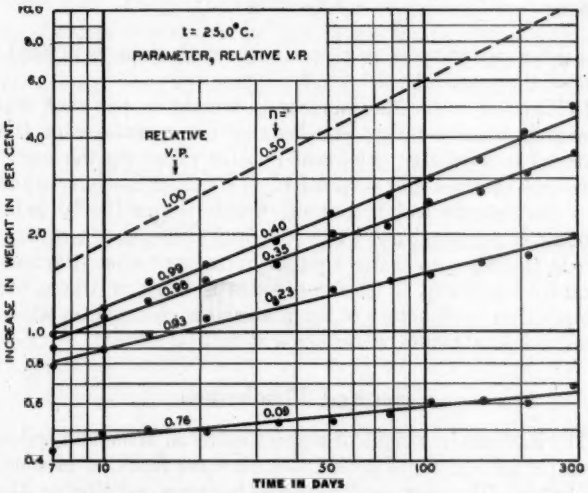


FIGURE 7. EFFECT OF RELATIVE VAPOR PRESSURE ON RATE OF WATER SORPTION BY RUBBER SHEETS

(Logarithmic plot of the data of Lowry and Kohman)

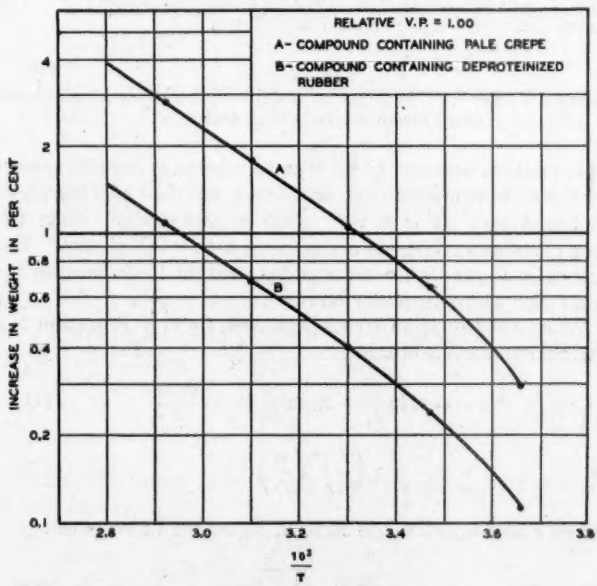


FIGURE 8. EFFECT OF TEMPERATURE ON RATE OF WATER SORPTION BY RUBBER SHEETS

where m = slope of curve

This equation may be combined with Equation 1 in the same manner as was Equation 4, giving,

$$\ln c = n \ln \frac{t}{t_1} + \left(\frac{m}{T_1} - \frac{m}{T_s}\right) + \ln c_1 \qquad (9)$$

The same variations in m as in n occur with changes in hardness of the material.

In distilled water the increase in weight in per cent will approach infinity unless checked by the resistance of the material to swelling. At lower relative pressures the vapor pressures external and internal to the rubber become equal at some definite water content, which is practically independent of temperature. The principal influence of temperature is, therefore, to hasten equilibrium, except where the temperature coefficient of the impurities is large or where the composition or structure of the material is changed, in which cases the equilibrium water content will be altered.

Effect of Thickness

The increase in weight of a sheet material after immersion in water for a definite period is an inverse function of sheet thickness. The per cent increase becomes infinite as the thickness approaches zero, but approaches zero as the thickness increases indefinitely. The graph of this relation is that of a rectangular hyperbola as shown by Figure 9. The quantities c and x are related as follows:

$$c = c_1 x_1/x \qquad (10)$$

where c = per cent increase in weight of thickness x calculated from measurements of c_1 and x_1

This relation appears to be true for sheets of infinite area or for sheets so prepared that water does not flow into the sheet at the edges. It is a very close approximation when the area of a sheet is large in comparison with its thickness. The curves in Figure 9 are not exactly straight lines because the areas were not sufficiently large.

When c of Equation 10 is substituted for c_1 in Equation 5, a general equation is obtained:

$$\ln c = n \ln \frac{t}{t_1} + n_1 \ln \frac{p}{p_1} + \ln \frac{c_1 x_1}{x} \qquad (11)$$

or

$$c = \frac{c_1 x_1}{x} \cdot \left(\frac{t}{t_1}\right)^n \left(\frac{p}{p_1}\right)^{n_1} \qquad (12)$$

When n and n_1 are taken as 0.50, Equation 12 becomes:

$$c = \frac{c_1 x_1}{x} \sqrt{\frac{t}{t_1} \cdot \frac{p}{p_1}} \qquad (13)$$

It thus becomes possible to describe the water-sorbing characteristics of a material by measuring the water sorbed by a thin sheet of the material after some known period of exposure to a constant vapor pressure.

To facilitate the comparison of one material with another, some sort of constant or "sorption coefficient" is desirable. In the case of sorption by thin sheets such a coefficient is not difficult to devise. Since the slope of the increase in weight *vs.* time curve in Figure 3 is a measure of the rate of sorption,

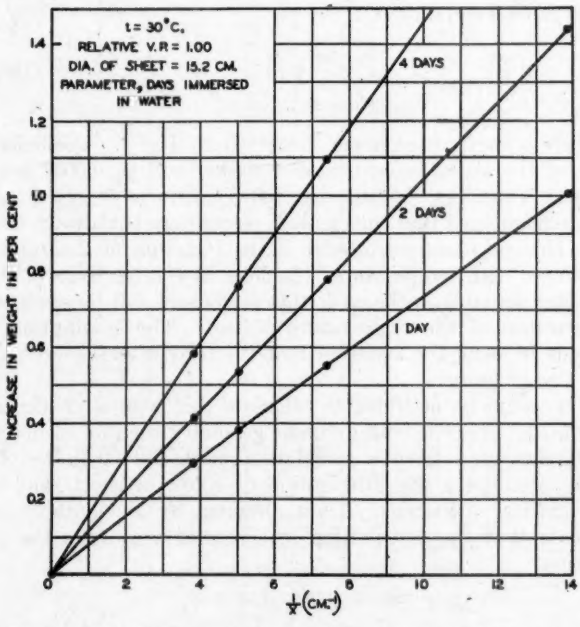


FIGURE 9. EFFECT OF SHEET THICKNESS ON RATE OF WATER SORPTION BY RUBBER SHEETS

the ratio $c_1/\sqrt{t_1}$ will be a constant for any given thickness. Since $c_1 x_1$ is also a constant at any given time, the rate $c_1/\sqrt{t_1}$ will be inversely proportional to the thickness, and the sorption coefficient, α, may be written:

$$\alpha = \frac{c_1 x_1}{\sqrt{t_1}} \tag{14}$$

Omitting the vapor pressure term and inserting α, Equation 13 will reduce to:

$$c = \frac{\alpha}{x}\sqrt{t} \tag{15}$$

When c is in grams per 100 grams of dry material, α will be expressed in cm./hour$^{1/2}$. The sorption coefficient for the

soft rubber described in Figure 3 is therefore 0.015 cm./hour$^{1/2}$ as compared with 0.0024 for ebonite and 0.026 for a good grade of phenol plastic at 30° C. This coefficient permits the comparison of different sheet materials at the same temperature. Equation 15 shows that the time required to sorb a given amount of water is proportional to the square of the sample thickness.

It has been found convenient to include vapor pressure in the coefficient in order to facilitate comparison of materials from data obtained at different temperatures. In such case the general equation is:

$$c = \frac{\alpha}{x}\sqrt{tp} \qquad (16)$$

where α is expressed in cm./hour$^{1/2}$/mm. Hg$^{1/2}$. Coefficient α for the above soft-vulcanized rubber will be 0.0027 cm./hour$^{1/2}$/mm. Hg$^{1/2}$ rather than 0.015 cm./hour$^{1/2}$. It should be remembered that the one-half power may not always hold for changes in vapor pressure if the structure of the rubber changes with temperature. As long as the hardness of the rubber remains unchanged, this coefficient will be obtained regardless of the temperature of test. The assumption is made in using the equation that the relative vapor pressure is always unity.

It would be desirable to calculate this type of coefficient from test specimens of different geometry such as a cube, a cylinder, etc. Such a calculation would be facilitated by data describing the distribution of water in sheets and in cylindrical specimens. Data obtained by the authors indicate that the distribution in sheets approximates the relation:

$$c = (m/x) + b$$

Lacking a precise means for calculating α for specimens of varied geometry, we must resort to experimental values. The weight of water sorbed per unit area as proposed by Boggs and Blake (*2*) will, however, give an indication of the amount such specimens will sorb although data obtained from sheets do not appear to be in sufficient agreement with those from cylindrical and cubical specimens for many applications.

In considering the practical application of these equations, it should be pointed out that the best results will be obtained if the sorption tests are made at the temperature and relative vapor pressure at which the material is to be used. Misleading results may be obtained if sorption tests are carried out at 70° C. on wire intended for use at 15° C. Not only may the physical characteristics of the insulation differ appreciably at the two temperatures, but changes affecting the sorption of water and the electrical characteristics may take place at 70° C. which are not perceptible at 15° C. The

hydrolysis, for example, of proteins and esters which may be present in rubber is greatly accelerated by increased temperature. As an illustration of some of these effects, data on the sorption of water at various temperatures by thin sheets of vulcanized pure gum rubber were obtained by F. S. Malm and G. G. Winspear of these laboratories (Figure 10). The curves indicate that chemical changes are taking place and

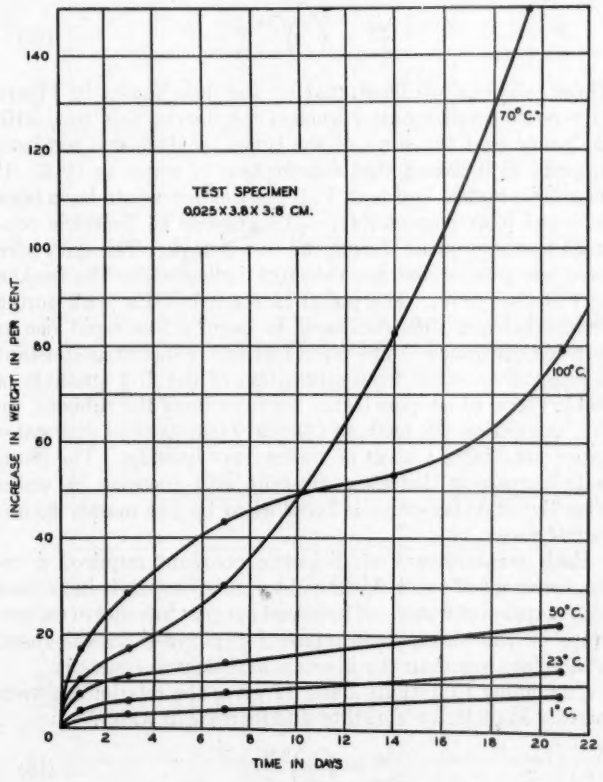


FIGURE 10. CHANGES IN RATE OF WATER SORPTION BY RUBBER AT ELEVATED TEMPERATURES

show that after a certain period the rate of sorption may increase markedly in rubber kept in water at elevated temperatures. After about 3 days water-soluble substances were formed at an accelerated rate in the sheet maintained at 70° C. In the sheet maintained at 100° C. additional vulcanization took place for several days before deterioration began. Water-soluble material continued to wash out at all temperatures during the test. It is evident that the data obtained at either 70° or 100° C. do not give a true picture of the performance of the rubber at 15° C.

Effect of Sorbed Water on Dielectric Constant

An important practical application of sorption data is their use in predicting the changes in the dielectric constant of a material which accompany the sorption of water.

When sheets of rubber are immersed in distilled water at constant temperature, the per cent increase in weight, c, is proportional to $t^{1/2}$, but the accompanying per cent increase in dielectric constant, $\Delta\epsilon$, is proportional to $t^{1/4}$. Hence,

$$\frac{\Delta\epsilon}{\Delta\epsilon_1} = \left(\frac{t}{t_1}\right)^{0.25} \tag{17}$$

These relations are illustrated by the data shown in Figure 11. Some soluble matter leached out during this test, with the result that the slope of the curve for dielectric constant dropped to 0.22 and that for sorption of water to 0.44. If no soluble matter had been lost, these slopes would have been 0.25 and 0.50, respectively. The increase in dielectric constant was very rapid during the first 2 days. The data here were less precise and are therefore indicated by the broken part of the curve. The power factor reached a peak during this period and then decreased to begin a less rapid rise as sorption continued. The rapid increase in dielectric constant is believed to result from adsorption of the first amounts of water vapor which penetrated the interior of the rubber. In this connection the authors (*8*) previously showed that water vapor penetrates a sheet of rubber very quickly. The parabolic increase in dielectric constant with increase in water after the first day or so is believed to be due mainly to absorbed water.

Each measurement of dielectric constant required a remeasurement of sheet thickness, as rubber expands in volume with sorption of water. The actual per cent increase in capacitance of the sheet, uncorrected for increase in thickness, is therefore less than the increase in dielectric constant.

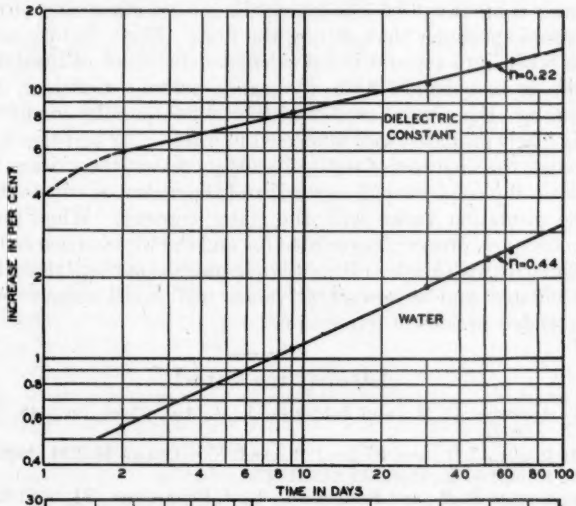
Combining Equations 2 and 17 gives the relation between increase in dielectric constant and increase in water.

$$\frac{\Delta\epsilon}{\Delta\epsilon_1} = \left(\frac{c}{c_1}\right)^{0.50} \tag{18}$$

where $\Delta\epsilon_1$ and c_1 are experimentally determined. This relation is illustrated in Figure 12, the data of which were obtained by combining the two curves in Figure 11. It is obvious that, if the relation between dielectric constant and water content is known, a measurement of dielectric constant alone will suffice to describe the water-sorbing characteristics of dielectric materials.

Different rubber compositions differ in the amounts of water they sorb and also in the effect of this water on the dielectric constant. In either case the curves, as in Figure 11, will be shifted along the ordinate but will maintain their respective slopes. In Figure 12 a larger increase in dielectric

constant per unit quantity of water will shift the curve upward on the graph in the same manner.



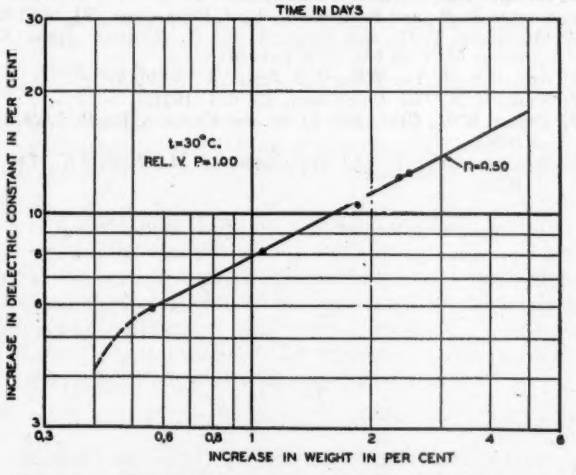


FIGURE 11 (*Top*). COMPARISON OF RATE OF INCREASE IN DIELECTRIC CONSTANT AND SORPTION OF WATER BY RUBBER SHEETS IMMERSED IN DISTILLED WATER

FIGURE 12 (*Bottom*). VARIATION OF INCREASE IN DIELECTRIC CONSTANT OF RUBBER SHEETS WITH SORBED WATER

Dielectric Constant of Insulated Wire

As with sheets, the greatest concentration of water in rubber-covered wire occurs in the outer layer of the insulation, decreasing rapidly toward the center. During the sorption process the insulation expands in volume, usually by

an amount approximating the volume of the water taken up. Furthermore, owing to alteration in the structure of rubber by wetting and drying, the time required to reach a given water content will be less during the second immersion of the redried specimen than during the first. These factors must be taken into account if the calculated behavior of insulated wire is to coincide with the experimental. Consider, for instance, the mutual capacitance of a two-parallel-conductor circularly insulated wire immersed in water. As sorption continues, the diameter of the insulation increases, the spacing between the conductors is altered, and the dielectric constant of the insulation varies with the water content. When these factors are properly accounted for and the wire is regarded as insulated, with graded rather than homogeneous insulation, the calculated and experimental values will check closely over extended periods of immersion.

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The Polymerization of Butadiene and the Production of Artificial Rubber

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The sole basis for the production of artificial rubber in Germany is at the present time 1,3-butadiene, $H_2C{:}CH.CH{:}CH_2$. Other diolefins, such as isoprene and 2,3-dimethylbutadiene, important during the War, have no longer any practical importance. The reason for this change to the basic raw material 1,3-butadiene, in place of the probable unit substance of natural rubber, isoprene, as the starting point of earlier technical processes, is attributable on the one hand to economic factors and on the other hand to the fact that artificial polymerizates of butadiene have particularly favorable properties.

The method ordinarily used at present for synthesizing butadiene can be found in text-books. It starts with acetylene and includes the following steps:

$$HC{\equiv}CH \longrightarrow H_2CHO \longrightarrow H_2CCH(OH)CH_2CHO \longrightarrow$$
$$H_2CCH(OH).CH_2.CH_2OH \quad H_2C{=}CH.CH{=}CH_2$$

Simpler and more economical processes would, of course, be of great interest. It seems questionable whether a new Russian process for preparing butadiene directly from ethyl alcohol vapor in the presence of certain contact agents will, with the complicated process shown above, be able to compete successfully, since it yields butadiene of only a low grade of purity, and high purity is a prerequisite for the favorable progress of polymerization.

In America at the present time, 2-chlorobutadiene, or chloroprene, is of outstanding interest among the diolefins which can be polymerized. Its synthesis has been developed from the discovery of Nieuwland in the United States that acetylene can be dimerized to vinylacetylene by cuprous chloride in hydrochloric acid. With hydrogen chloride, vinylacetylene forms chloroprene:

$$2HC{\equiv}CH \longrightarrow H_2C{=}CH.C{\equiv}CH \longrightarrow H_2C{=}CH.CCl{=}CH_2$$

Chloroprene is produced by E. I. du Pont de Nemours and Company, and is polymerized to so-called Neoprene rubber, which, because of its oil resistance, has found various applications for special purposes. In Germany, however, it is of no importance.

The formation of vinylacetylene from acetylene suggests the application of this elegant reaction to the preparation of butadiene, which should be formed by partial hydrogenation of vinylacetylene. This would simplify fundamentally the synthesis of butadiene. In so far as can be judged by published information, this problem has been solved in a scientific sense; however, certain technical difficulties have heretofore prevented the use of this synthesis in a practical way.

Aside from the production of cheap raw materials, the polymerization of diolefins to technically useful artificial products closely resembling rubber is the major problem in synthesizing rubber. On standing, chloroprene polymerizes readily,

without any further treatment, to Neoprene rubber, which it is unnecessary to discuss further at this time. On the other hand, in the case of butadiene and other diolefins, polymerization must be effected artificially by suitable means since, in spite of the fact that these substances do polymerize spontaneously, the process is uncertain in starting and is uneconomical because of the long time required. A wide variety of substances is known to induce polymerization, including acids, metal halides, etc., with the aid of which butadiene and its homologs polymerize easily. The resulting products may differ greatly in their properties. Besides the rubber-like products which efforts have been made to produce, oils, resins, and other products with undesirable properties may be formed. The various rubber-like polymerizates ordinarily differ greatly in certain technically important properties, *e. g.*, in their autoöxidizability. In spite of the great number of possible methods, only two processes for the polymerization of butadiene have been developed successfully, *viz.*, polymerization by metallic sodium and the so-called emulsion polymerization.

Polymerization by metallic sodium, the end-product of which, *viz.*, butadiene sodium rubber, has as "Buna" given the name to this whole group of rubber-like polymers of butadiene, depends on the following observation.

When a small piece of metallic sodium is introduced into liquid butadiene or into butadiene vapor, a polymerizate is formed around the sodium more or less rapidly, depending on the purity of the butadiene. This growth takes place in the form of a small branched tree. In the end all the butadiene is transformed into a mass of rubber-like product surrounding the metal. This phenomenon is particularly striking when the metal is suspended in the vapor of butadiene, for under these conditions the gradual disappearance of the liquid butadiene below and the simultaneous formation of the polymerizate in cluster form above is most evident.

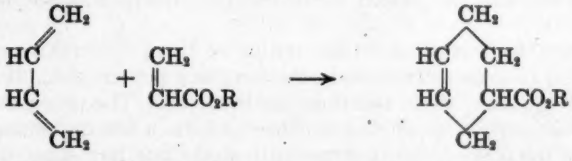
Technical processes for polymerizing butadiene by means of metallic sodium are adaptations of this fundamental experiment. The details of these processes depend on two factors which are of no particular interest in this discussion. The advantage of this type of polymerization lies in the possibility of working in a concentrated system, and the resulting economical utilization of the volume required for the reaction. A disadvantage is the fact that it is not always easy to remove with any degree of certainty the very large quantity of heat of polymerization which is evolved. However, the process yields firm masses of Buna, which can be sheeted out, without any preliminary treatment, on mills by the ordinary technic used in the rubber industry. It has been found possible to modify the properties of the polymerizates, particularly their viscosity under standardized conditions, in a reproducible way, by adding certain reagents during polymerization. Naturally this is of the utmost importance, since subsequent processing of the Buna calls for a material of high or low viscosity, depending on the particular use to which it is put. The various types of Buna which can be made in this way are designated by a number system which represents the viscosity, and they appear on the market with these distinguishing numerical characters.

The effect of foreign substances during polymerization on the viscosity of the resulting polymerizates depends on their effect on the degree of polymerization, *i. e.*, on the size of the molecules. The manner in which these substances act will be discussed later.

Emulsion polymerization is an attempt to duplicate natural latex. As is well known, natural rubber occurs as an emulsion in the form of extremely small globules in the milky juice, or latex, of certain plants. A similar emulsion can be prepared by suspending butadiene in water in presence of suitable emulsifying agents, *e. g.*,

sodium oleate, and polymerizing by certain catalysts. In this case all peroxides, including hydrogen peroxide, are polymerizing agents. The product is a "rubber milk" which closely resembles natural latex, and from which rubber can be separated as a coagulum by treatment with acids, as in the case of natural latex. The advantages of this process lie in better control of the dissipation of the heat of polymerization, and also in the fact that the initial product is a latex, since the latter is important in technical processes which depend on the direct use of latex. Thus one of the uses of such latex is in the production of certain kinds of artificial leather. On the other hand a disadvantage of the emulsion polymerization compared with polymerization by sodium lies in the far greater volume required for the reaction, since the latex is only in part composed of rubber.

Of particular interest from the scientific point of view is the fact that most types of artificial rubber formed by the emulsion process are mixed polymerizates, *i. e.*, other polymerizable substances, especially so-called "vinyl substances" are added to the butadiene before the latter is polymerized. Among these vinyl substances are esters of acrylic acid, acrylic acid nitrile, and styrene. In this connection it is a remarkable fact that whereas these typical mixed polymerizates of high molecular weights are formed directly by the emulsion polymerization process, they are not formed when mixtures of butadiene and the substances mentioned are simply brought together in concentrated form. Under these conditions the smoothly progressing addition of one molecule of butadiene to one molecule of the vinyl substance is always the predominant reaction, in accordance with the scheme of the so-called diene synthesis:



In polymerization by the emulsion process, butadiene molecules and vinyl molecules link together in chain formation to large molecules, according to the general scheme:

$$--(Bu)_m-(VS)-(Bu)_m-(VS)-(Bu)_o-----$$

where Bu is a molecule of butadiene and VS is a molecule of the vinyl substance, and where, for example, a molecule of acrylic ester may lie between two butadiene molecules, giving the particular internal structure represented by the following scheme:

$$-CH_2-CH=CH-CH_2-CH_2-\underset{\displaystyle CO_2R}{\underset{|}{CH}}-CH_2-CH=CH-CH_2-$$

The underlying causes of this difference in the course of the reaction in a concentrated system and the emulsion reaction are not even today clearly understood. In any event, it is of no decisive importance whether, in the mixed polymerization reaction, the components are present in equivalent quantities, for whatever the conditions, butadiene predominates as a constituent of the product.

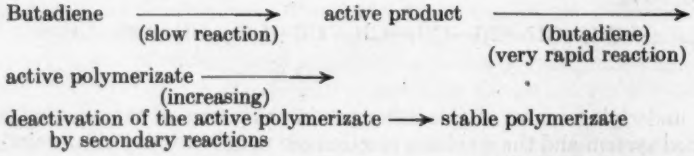
The trademarks of the particular types of Buna prepared by these polymerization reactions are designated by letters of the alphabet, which as a matter of fact indicate the particular vinyl derivative condensed with butadiene. These Buna products are called "alphabetic Bunas" to distinguish them from "numerical Bunas."

From a practical point of view, various problems connected with capacity for vulcanization, aging, nerve, resistance to abrasion, elasticity, etc., are involved in the foregoing brief discussion. Heretofore it has been possible to attack these problems only in an empirical way, and therefore they are likely to remain for the present within the domain of the technical laboratories and testing departments, which alone have at their disposal the necessary means for extensive experimentation. Aside from these centers of activity there have been no substantial results forthcoming from these investigations.

With regard to the quality which has been obtained, it may likewise be said with confidence that the era of "substitute" rubbers, with all the unsatisfactory experiences which were encountered during the first period when rubber was synthesized industrially during the War, is finally past. As a matter of fact still further improvements in the inherent quality compared with natural rubber are quite possible in view of the superior results already obtained with respect to the oil resistance and abrasion resistance of Buna.

For the investigator there are other highly interesting problems connected with these polymerization processes. Of these problems, that of the mechanism of the polymerization reactions lends itself particularly to a discussion at the present time. This problem is synonymous with the problem of the manner in which the molecules originally present grow during polymerization from the small molecules of the starting material to the giant molecules of the final rubber. That a growth in size of the molecules takes place, whereby one butadiene molecule after another becomes linked together, and not a sudden combination of many molecules, is unquestionably the case, as judged by the simple principles of the kinetics of the reaction.

The question then arises as to the nature of these "growth reactions" in the polymerization processes discussed in the foregoing paragraphs. It seems certain at least that unusually rapid reactions are involved. The processes follow in all cases the same course, *i. e.*, there is on the one hand a low molecular starting material, and on the other hand an apparently immediate formation of an extremely high molecular product. No intermediate stages in the polymerization have been observed. Since, however, most polymerization processes do not take place instantaneously, but always require a certain time, it must be concluded that the actual polymerization is preceded by a "starting reaction," which takes place slowly, and by which the butadiene is transformed into a very reactive state. The velocity of the process as a whole is therefore governed by the velocity of formation of the so-called "active centers" by the initial reaction. The following scheme shows the process in complete form.



As to the nature of the reaction whereby the butadiene is activated, a general interpretation applicable to all polymerization reactions cannot be offered. Many authors believe that the formation of some kind of radical must be involved, perhaps of the kind which it is customary to illustrate on paper as a setting up of double bonds, thus:

$$H_2C{=}CH{-}CH{=}CH_2 \longrightarrow {-}CH_2{-}CH{=}CH{-}CH_2{-}$$

The energy necessary for the establishment of these double bonds might be furnished by certain reactions of the polymerizing agent which is added, *e. g.*, by spontaneous decomposition of peroxides in the case of emulsion polymerization. The "free" valences then draw the ends of the neighboring butadiene molecules closer to them, as a result of which units containing two or three butadiene nuclei are formed. In every case these structural units carry at their ends active centers with "free" valences. The molecule then continues to grow according to the same principle, until finally the free valences on the ends disappear irreversibly as a result of a secondary reaction. A whole series of such possibilities can be imagined. It may be a question of an oxidation reaction or even a mutual saturation of two "free" valences. Then again a so-called "dismutation" of radicals is within the realm of possibilities.

In taking this point of view it does not matter whether or not one assumes the presence of free radicals in the ordinary sense or whether one assumes other forms of butadiene activated by an increase in energy. As a matter of fact, many intermediate possibilities between the two concepts are possible. Mechanisms of this character have been discussed frequently in the last few years, and have been studied from the point of view of the kinetics of the reaction.

Unquestionably such views are correct, at least in principle, for certain kinds of polymerization processes, *e. g.*, the emulsion polymerization reaction. It is difficult, however, to confirm them experimentally, except by a study of the kinetics involved.

However, that polymerization may take place by a wholly different mechanism is proved by extensive experiments which the present author and a large number of collaborators have carried on during the last ten years on polymerization by alkali metals. This work has shown that the active centers and other active parts of the growing molecules are organic alkali metal compounds.

These facts could not be learned directly from a study of the reaction between sodium and butadiene, since all the reactions take place so unusually rapidly that it has been impossible to distinguish the individual steps. If it is desired to obtain true facts on the course of the reaction, it is necessary to employ various artifices to retard and moderate the general course of the reaction. This can be accomplished:

1. By recourse to 2,3-dimethylbutadiene, which is far slower to react with metals than is butadiene
2. By replacement of sodium by another metal, such as lithium, which in many respects is superior to sodium for such experiments, and
3. By operating in dilute (ether) solutions.

Under these conditions there is no difficulty in showing that a di-lithium addition compound is the initial product of the reaction of dimethylbutadiene and lithium, and that this addition product readily adds another molecule of diolefin, so that the following two compounds are obtained together as initial products:

$$LiCH_2C(CH_3):C(CH_3)CH_2Li$$
$$LiCH_2C(CH_3):C(CH_3)CH_2CH_2C(CH_3):C(CH_3)CH_2Li$$

These lithium compounds are capable of increasing in size further by combination with more dimethylbutadiene by the metallo-organic ends of the growing molecule adding each time to dimethylbutadiene, so that products of the general formula:

$$Li[CH_2C(CH_3):C(CH_3)CH_2]_nLi$$

are formed, where the greater the quantity of butadiene, the higher the numerical value of n. It can also be readily shown that in the course of such an experimental

reaction the low molecular substances which are first formed gradually disappear in favor of compounds with higher molecular weights.

Consequently, in this case the initial reaction is the formation of an organic alkali addition compound of lithium and dimethylbutadiene, and as the growth reaction, the continuous organo-metallic synthesis by addition of a lithium compound to the diolefin. By the choice of suitable experimental conditions, it was possible to retard all reactions to such an extent that they could be observed readily.

In the polymerization of butadiene by sodium, a disodiumbutadiene is likewise formed as an initial product, as it is possible to demonstrate conclusively. This reaction is, however, very slow, because it takes place only in the surface of the sodium. The disodium compound of butadiene then reacts with extraordinary rapidity with the butadiene present in the highest concentration, and only when the butadiene has disappeared completely is the organo-alkali compound formed in any considerable quantity. It has been found possible, by means of certain artifices, to control the course of this reaction so that it is strictly analogous to that which takes place with dimethylbutadiene. Such an artifice is, for example, to "offer" to the butadiene previously prepared alkali alkyls of the general formula RNa, RK, and RLi in high concentration. In this case addition products of the general formula:

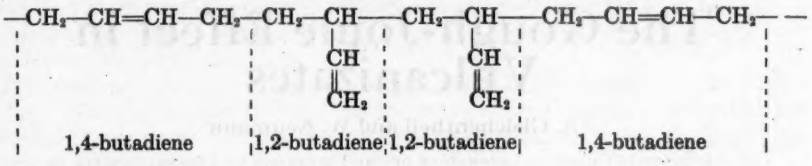
$$R \cdot (\text{butadiene})_n \text{ Na (K, Li)}$$

are formed. With small proportions of butadiene, the products are of relatively low molecular weight, but they are capable of further growth by subsequent addition of more butadiene. This has been proved quite conclusively. By using a large excess of butadiene, the polymerizates which are obtained have thoroughly rubber-like properties, whereas with small proportions of butadiene all intermediate steps down to very small molecules with few butadiene residues are obtained. The ease with which butadiene is polymerized by sodium depends therefore on its very unusual ability to react extremely rapidly with organic alkali compounds, with formation of addition products.

With the aid of this theory, it may be readily understood to what extent additions of certain reagents can be made to the polymerization mixture and the viscosity of the polymerizate be thus regulated at will. The substances added for this purpose represent a type which can react with a certain velocity with the organo-alkali ends of the growing molecules. In this reaction the alkali disappears from the organic compound, and the remaining molecule thereby loses its capacity for further growth. Obviously then the total length of the chain molecule of rubber depends on the average frequency with which such a metallo-organic end of the molecule reacts with butadiene molecules before it is irreversibly destroyed through transformation by the accessory regulator which has been added. It resolves itself then into the simple question of the relative velocities of the reactions of the organo-alkali butadiene compound on the one hand and of the so-called regulator on the other. This relation can be controlled within wide limits by changing quantity and nature of the regulator, and in this way it becomes possible to prepare polymerizates of widely differing molecular weights.

Studies of the reactions of organo-alkali metal compounds and butadiene has also given an insight into the structural principles of the polymerizates. As a result of ozonization experiments, natural rubber is known to be a practically uniform 1,4-polymerizate. The ozonization of the sodium polymerizate entails difficulties which have up to the present time prevented any such clearly defined statement as is possible about natural rubber. According to the results of certain syntheses, it can merely be concluded that in the alkali polymerizates a part of the butadiene

is built into the molecule in 1,2-form and another part in 1,4-form, so that a section of the whole molecule may in principle be of the following character:



1,2 and 1,4 vary in a wholly irregular way.

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The Gough-Joule Effect in Vulcanizates

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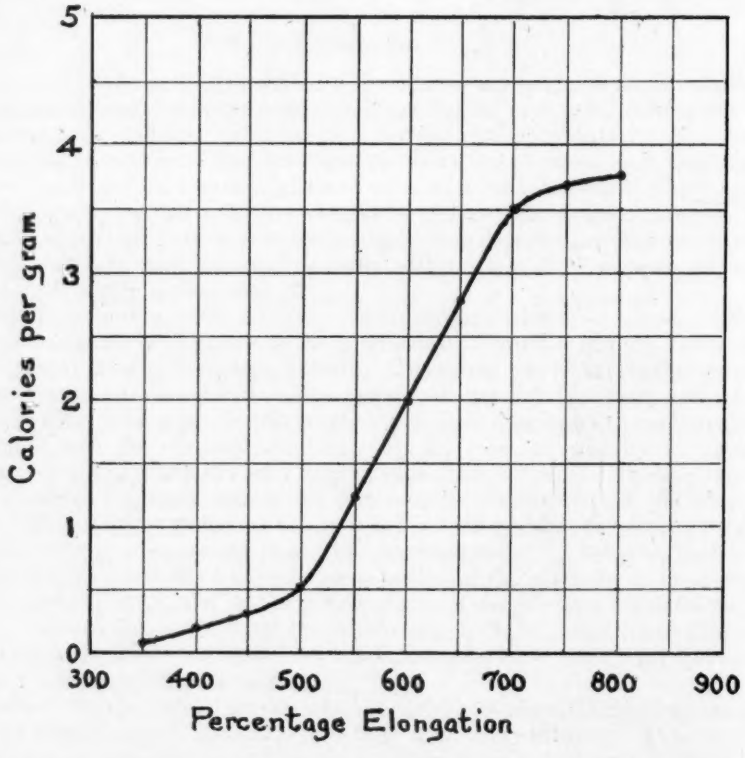
Since the phenomenon now known as the Joule effect was first measured, only a few investigators have concerned themselves with this phenomenon. Hock,[1] one of these investigators, measured the heat which is evolved by raw rubber when stretched, and found that the quantity of heat evolved is proportional to the degree of elongation. When, therefore, the quantity of heat is plotted against the percentage elongation, a straight line is obtained.



The present authors have measured the heat evolved when vulcanized rubber is stretched, the method being to stretch a strip of rubber in a calorimeter filled with mercury.

It was found that under these conditions the trend of heat evolution found by

Hock did not hold true over the whole range of elongation; there was instead a relatively slow increase in heat evolved with increase in elongation, then a more rapid and at the same time uniform increase over a higher range of elongation. Finally, at the highest degrees of elongation, *i. e.*, above 700 per cent, the increase became less again (see diagram).

These measurements were made on a latex vulcanizate containing 2 per cent of sulfur. It is obvious that the heat evolved at the highest degrees of elongation was 3.8 calories per gram, a value which seems to confirm earlier estimations of approximately 7 calories for the heat of fusion of rubber, since it may be safely assumed that only about 60 per cent of the total quantity of substance is crystallized. The relatively slow increase in heat evolution during low stages of elongation may be attributed to the fact that there is at first an appreciable entropy effect;[2] at higher degrees of elongation, *i. e.*, through the linear part of the curve, the far stronger effect of the heat tone of crystallization predominates. In the upper part of the curve the maximum possible crystallization is approached, so that further stretching evolves relatively little more heat.

The experiments are being continued, with special attention to the evolution of heat as a function of the degree of vulcanization and the type of vulcanizate.

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[2] Guth and Mark, *Naturwissenschaften*, **25**, 353 (1937)

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Structure of Stretched Rubber

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University of Vienna

Investigations of the micellar structure of fiber substances have given rise to two theories. The older theory (Meyer and Mark, 1930; Mark, 1932; Siefriz, 1934; Meyer, 1930; and Nägeli, 1928) considers the micelles as separate crystallites, between which lie the intermicellar spaces. The micelles consist of "Hauptvalenzketten"* bound together along their length by homeopolar bonds and in the transverse direction by van der Waals' forces, the intermicellar binding being also attributed to van der Waals' forces. The original model suggested in work published by Meyer (1930) for cellulose depicts the micelles arranged like bricks in a wall (Fig. 1), and doubtless this is the simplest explanation of the x-ray results. But it is difficult to understand how such an arrangement can give a micellar structure its peculiar mechanical properties, and further how it is possible, when both inter- and intramicellar cohesion are attributed to the same type of force, to cause by swelling experiments an enlargement of the intermicellar spaces, while the "Hauptvalenzketten" remain unaffected.

An alternative theory has been put forward by Gerngross, Herrmann, and Abitz (1930), Astbury (1933), Frey-Wyssling (1936), and Guth and Rogowin (1936). These authors suppose that a given "Hauptvalenzkette" is not confined to a single crystalline region but may stretch through more such regions. In general, the arrangement of the neighboring chains will be truly lattice-like, but a chain may lie at too great a distance from its neighbors or not lie exactly parallel to them, so that the structure as a whole will show statistically distributed spaces. In Fig. 2 ordered crystalline regions may be distinguished (drawn in thick line), but their significance is physically different from that of the crystallites of the Meyer model. They are not self-contained units; the whole system is linked together due to the "Hauptvalenzketten" extending beyond a single micelle. Astbury considers that, in a substance of high molecular weight of a type capable of swelling, that part which produces the x-ray spectrum is the concentration center of a complicated network of thread-like molecules. He draws an analogy between micellar structure and the secondary structure of Zwicky. He suggests that it is possible that micellar systems, which are characterized by a mixture of perfection and imperfection, are the counterpart in compounds of high molecular weight of the well-known mosaic structure of the more familiar crystals. Frey-Wyssling is of the opinion that the micelles, growing together, enclose lens-shaped spaces running parallel to the fiber axis. Between these intermicellar spaces are small rod-shaped regions of undistorted lattice, which are the so-called micelles of the earlier work (Fig. 3). In this figure, which gives a pictorial representation of Frey's theory, the statistically distributed hollow spaces are shown black; some of these are enclosed in undistorted crystalline regions. A lamellar structure consisting of superimposed monomolecular layers suggested by Sponsler and Dore (1930) has been shown to be untenable from the work on double refraction by Baas-Becking and Galliher (1931).

In order to investigate further the micellar structure the effect of "higher orien-

* Long-chain molecules of high molecular weight.

tation," which up till now has been little used in such cases, was studied (Mark and Kratky, 1937). By this is meant an ordering of the crystalline regions so that they are parallel not only to the long axis, but also in a second crystallographic direction. Figure 4 represents a cross section through a fiber system, the short lines being sections of the single chains. Regions which are exactly ordered, others not completely ordered, and hollow spaces are shown. The *a* and *c* axes lie in quite different directions in different parts of the fiber, but the *b* axis (fiber axis) is always in approximately the same direction, *i.e.*, in our diagram, perpendicular to the plane of the paper. With the appearance of "higher orientation," the direction of the "Hauptvalenzketten" remains as before, but a parallel ordering of the *a* and *c* axes occurs. (The lines will be parallel to one another.) The effect was first observed by Mark and von Susich (1928) for stretched rubber; the intensity of the interference pattern alters in a characteristic way according to whether the radiation is directed parallel or perpendicular to the direction of stretching. With the

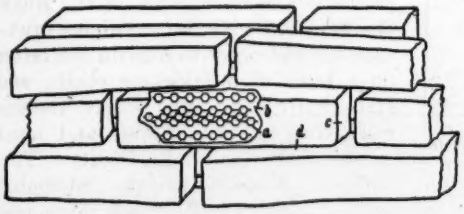

Figure 1—Micellar Structure after Meyer. a, Hauptvalenzketten; b, Intramicellar Regions; c, Intermicellar Holes; d, Intermicellar Long Spaces.

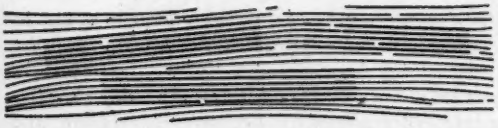

Figure 2—Micellar Structure after Guth and Rogowin.

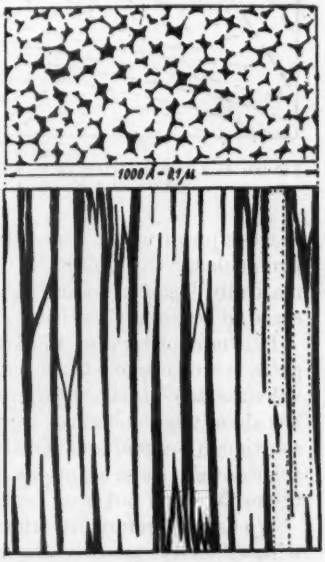

Figure 3—Cross Section and Longitudinal Section Through an Intermicellar System (A. Frey-Wyssling)

radiation perpendicular to the direction of stretching, the spot (200) is most intense, (210) is weaker, while (002) and (012) are feeble, the order being reversed when the radiation parallel to the direction of stretching, (002) is very strong, (012) less so and (200) and (210) are quite weak. From such diagrams Mark and von Susich have recalculated the rhombic elementary cell of rubber to be $a = 12.3$, $b = 8.1$ (fiber axis), and $c = 8.3$ A.

A tentative structure with eight isoprene residues in the unit cell, and based on a series of isoprene chains, has been put forward. From measurements of the breadths of interference patterns, Hengstenberg (1928) estimates the dimensions of the rubber micelle to be of the order $600 \times 500 \times 150$ A. Recent work of Sauter

(1937) is in substantial agreement with this structure, although the dimensions of the unit cell are found to be slightly larger: $a = 12.60 \pm 0.05$ A., $c = 8.91 \pm 0.05$ A., $b = 8.20 \pm 0.05$ A. It has been further suggested by Meyer and Mark (1928) that the elementary cell for rubber must be shorter than the length of a single molecule.

Other examples of "higher orientation" are shown by the cell wall of *Valona ventricosa*, where it appears with growth, and by mechanically worked cellophane. From the results of a number of experiments (Mark and von Susich, 1929; Burgeni and Kratky, 1929; Eggert and Luft, 1930; Hess and Trogus, 1930) it was concluded that the lath-shaped micelles become oriented by rolling so that their longest and second longest edges lie in the plane of rolling. Mark and Kratky (1937) consider that sliding in the lattice or rotation of the single chains cannot give rise to "higher orientation." In order to explain the latter on a basis of interlocking chains and statistically distributed spaces, the micelles must be lath-shaped and must possess a certain individuality. This will occur if the statistically distributed spaces appear more frequently in the direction of two crystallographic axes perpendicular to the fiber axis. Then the small regions of undistorted lattice will automatically become bound together by lattice forces into lath-like forms and will cease to be isolated entities.

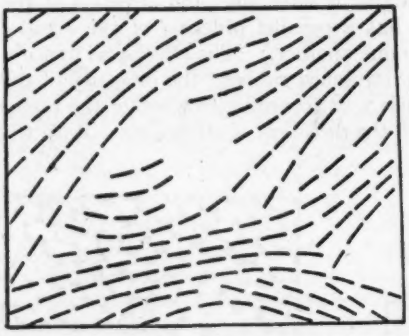

Figure 4—Cross Section of a Fiber System (Mark and Kratky)

It is now interesting to discuss whether the building up of such lath-like aggregates is a characteristic of naturally occurring conditions, or whether the "Hauptvalenzketten" themselves are able to build up such micelles from solution. It has already been observed that hydrated cellulose films obtained from xanthogenate solutions (Burgeni and Kratky, 1929) show "higher orientation," but it might be argued that these solutions were extremely concentrated and that the micelles themselves had not been broken up.

We have therefore investigated a series of very dilute solutions of a rubber soluble with difficulty, made by drying the latex (braun-gelb) in benzene, chloroform, and carbon tetrachloride, these solvents being chosen with a view to examining a possible influence on "higher orientation." The rubber only partially dissolved after shaking for 1–2 weeks on a machine, so that the objection that the micelles have not been split up can still be made. For comparison, solutions of an easily soluble rubber (first latex crepe) were also made in the same solvents. To make the films actually employed, the dilute solutions were poured on to a glass plate or mercury surface, when the solvent evaporated and left a thin film of rubber; by repeating the process several times the films could be made about 0.1 mm. thick. They were then dusted with rice powder, after which they could be stripped from the underlying surface. The x-ray photographs were taken on a fiber camera, the plate-specimen distance being 35 mm. and the collimator 0.8 mm. in diameter. The rubber film under investigation was held in a special extension apparatus.

The x-ray tube was a Siemens Strukturröhre, with a copper anticathode and Ni filter, running at 45 kv. and 15 ma. Under these conditions the exposure time was of the order of 6 hours.

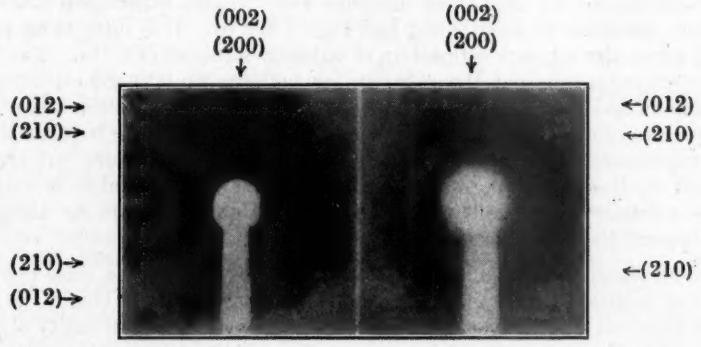

Figure 5a

Figure 5b

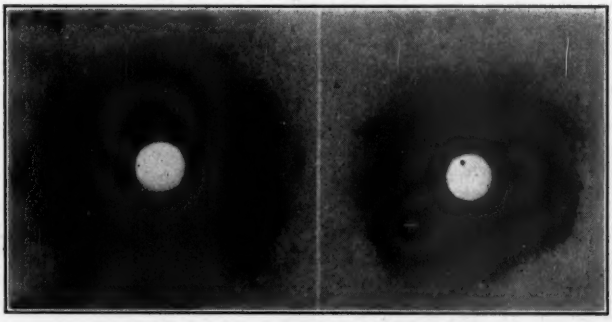

Figure 6a

Figure 6b

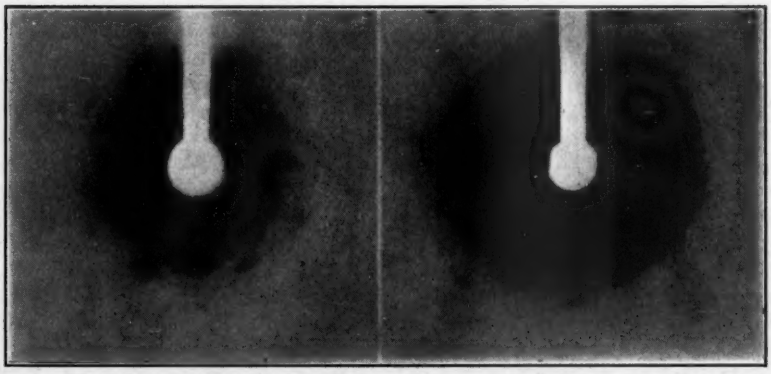

Figure 7a

Figure 7b

All the films derived from these solutions show "higher orientation" for x-rays on extreme extension to about 700% (see Figs. 5 and 6). It is interesting to note that the effect also appears with a film of vulcanized rubber (Fig. 7). The results of this work establish that the capacity for building up lath-shaped micelles in the way described is an intrinsic property of the "Hauptvalenzketten" themselves.

The picture of micelle structure here developed is intermediate between the two formerly proposed theories. The micelles are of lath-shaped form but probably not closed on all sides, and possess, on account of their shape and of their transverse bindings, a definite individuality, even though the "Hauptvalenzketten" themselves extend beyond the sphere of single micelles.

We have pleasure in thanking H. Mark and O. Kratky for their continued advice and assistance, and their interest in the investigation. One of us (C. J. B. C.) is indebted to Professor Mark for extending to him the hospitality of his Institute and to the University of London for a traveling studentship which made the work possible.

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[Translated for Rubber Chemistry and Technology from the Recueil des Communications du Congrès International du Caoutchouc, Paris, pages 203–207, June, 1937.]

Azo Dyes Derived from Rubber

Rodolfo Low

At one time the greater part of the rubber used in industry was in the form of wild rubber, and although it is true that even under these circumstances rubber possessed the valuable properties which make it one of the most useful of materials for the widest variety of applications and in general indispensable, it nevertheless varied greatly. This latter fault not only made it difficult to manufacture rubber goods satisfactorily but limited the field of applications of rubber. Then again, sufficiently large quantities of the most useful raw material could not be obtained regularly.

In contrast to this, the progress which has been made up to the present time in the cultivation of rubber has put industry in possession of a uniform product which is available in quantities sufficient to fulfil all needs. This has made it possible not only to manufacture rubber products in a more satisfactory way, but also to increase to an unforeseen extent the number of applications of rubber.

Moreover, when it is realized that crude rubber is a relatively cheap material, it will be evident why chemists are busy utilizing it for the production of derivatives which, because of new and valuable properties, will necessarily find wide fields of application. This is only one instance of the constant attention which the chemist gives to the possibility of transforming materials which nature has bestowed upon us into other materials of still greater benefit to humanity.

It will be found that for this reason the number of derivatives of rubber has increased during the last few years. It is sufficient to call to mind the various chlorinated rubbers which pass by the commercial names of Duroprene, Tornesit, Tegophan, Pergut, and Dartex; the cyclorubbers, such as sulfocyclorubbers and Thermoprenes; condensation products of rubber with benzyl chloride; polyhydroxyrubbers, and finally compounds such as hydrorubbers, which owe their lack of technical applications up to the present time to the high cost of hydrogenation rather than to any fault in properties.

It is interesting to observe that all these products were originally studied from the purely theoretical point of view. Chlorinated rubber was the outcome of a study of the reaction of rubber and halogens. Cyclorubbers were obtained in a study of the isomerization which rubber undergoes by the action of heat and various chemical reagents. The investigations of Pummerer and of Staudinger on the hydrogenation of rubber, carried on with the sole aim of obtaining information which would make it possible to establish the constitution of rubber, are, of course, well known. Certainly these investigators did not even suspect that the hydrorubbers which they obtained would have excellent properties which would some day result in their being used technically.

The present work is likewise a theoretical study; it deals with the manner in which the bromide of rubber reacts with certain aromatic derivatives. This is of course no drawback to the technical utilization of the dyes which have been prepared in the work. On the contrary, it is hoped to find means of improving their methods of preparation and of finding ways in which they can be used industrially, although it will be possible to accomplish this only after various obstacles have been

surmounted. If success is attained, the reward will be an increase in the number of derivatives of rubber which are of use technically.

Present knowledge of the constitution of rubber has established the fact that its molecule is composed of a great number of isopentene groups:

$$\cdots\cdots\text{—}CH_2\text{—}\underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}}\text{=}CH\text{—}CH_2\text{—}\cdots\cdots$$

formed by 1,4 polymerization of isoprene, and which will be designated, in accord with Pummerer, as the small rubber equivalent. All properties of rubber conform to this constitution which, in virtue of the fact that there is a double bond for each C_5H_8 group, can add such widely different substances as halogens, hydrogen halides, thiocyanogen, hydrogen, tetranitromethane, and nitrosobenzene. However, in some cases it is very difficult or even impossible to obtain an addition product corresponding exactly to the theoretical formula. This is the case, for example, with the thiocyanogen addition product, which agrees exactly with the theoretical formula only if it is prepared under certain conditions which are very difficult to reproduce.

According to Gladstone and Hibbert,[1] who were the first to study systematically the action of halogens on rubber, an addition product with bromine, the composition of which corresponds exactly to the formula $(C_5H_8Br_2)_x$, can be obtained readily by brominating a chloroform solution of rubber and evaporating the solvent. Later, C. O. Weber[2] came to the same conclusion. In this case he treated a chloroform solution of rubber with bromine and precipitated the bromide by alcohol.

Subsequent to these classic works, a large number of studies of rubber bromide have been published, the greater part of which had as their objective the quantitative determination of rubber in the form of its bromide. It is of interest to note that the results of the various authors do not agree, and in almost all cases the values are too high, because substitution products are formed at the same time as the addition product. As a result rubber is no longer determined quantitatively in the form of its bromide.

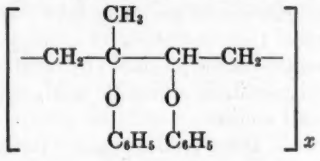
This brings up the question whether it is possible to obtain a bromide which conforms to the theoretical formula, as described by Gladstone and Hibbert[1] and by Weber,[2] or whether it is possible that this bromide has some formula other than $(C_5H_8Br_2)_x$, as indicated by later investigations on the determination of rubber. There is no doubt that the bromide mentioned can be prepared, and since the time of Weber chemists have obtained the same substance. The present author has been able to obtain a rubber bromide of the formula $(C_5H_8Br_2)_x$ containing 70.04 per cent of bromine (theoretically 70.13 per cent), but only by working under strictly controlled conditions which are not clearly defined in the early works cited above. The results of these experiments will be published in a forthcoming publication.

In studying the properties of his rubber bromide, Weber[3] proved that it reacted with phenol, with evolution of hydrogen bromide. This reaction can be represented by the following equation:

$$(C_5H_8Br_2)_x + 2C_6H_5OH \longrightarrow [C_5H_8(C_6H_5O)]_x + 2HBr$$

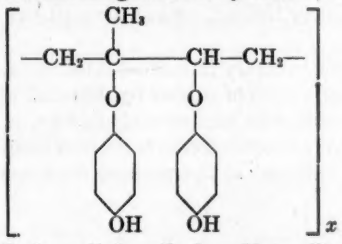
This formula agreed consistently with the analytical results. Similar reactions were obtained with cresol, thymol, resorcinol, naphthol, etc. On the other hand, according to Weber, phenolic ethers do not react with rubber bromide. From this fact Weber concluded that it is the hydroxyl group of phenol which reacts with the

bromine in rubber bromide, with formation of a phenolic derivative of the formula:



which is that of an ether.

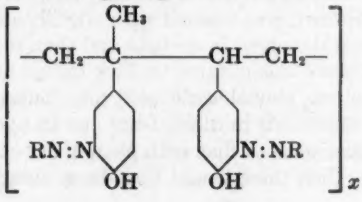
A quarter of a century later, Fisher, Gray, and McColm[4] studied this reaction further. The attention of these investigators was drawn to the solubility of the phenolic derivative in alkalies, which seemed to indicate the existence of free phenolic hydroxyl groups. To prove this supposition, the phenolic derivative of rubber was methylated, and a dimethyl ether was thus obtained. The formula of the phenolic derivative was not that assigned to it by Weber,[3] but the following:



i. e., the formula of a *dihydroxydiphenylhydrorubber*. Furthermore these authors proved that the reaction proceeds much better in the presence of anhydrous ferric chloride as catalyst. The reaction between rubber, bromide, and phenol would appear then to be a special case of the Friedel and Crafts reaction.

Soon after this, Geiger[5] repeated this same reaction, and succeeded in benzoylating the dihydroxydiphenylhydrorubber; this benzoylation led to the disappearance of the solubility in alkalies. Geiger also discovered that, contrary to the statement of Weber, rubber bromide reacts with phenolic ethers, although the reaction is much slower in this case.

All this shows definitely that the phenolic derivative of rubber has the constitution proposed by Fisher, Gray, and McColm,[4] but it still remains to be ascertained whether the phenol unites in the *ortho*, *meta*, or *para* position. The solubility in alkalies and the possibility of obtaining a dimethyl ether and a dibenzoyl derivative demonstrate sufficiently well that the phenolic derivative of rubber contains free phenolic hydroxyl groups. However, Geiger,[5] with the aim of extending the number of reactions in support of this, attempted to combine the phenolic derivative of rubber with diazonium salts. If free phenolic hydroxyl groups are really present in the compound, a coupling reaction of this kind should be possible, and as a result one should obtain azo dyes, the molecules of which would be derived from the rubber molecule. The results obtained by Geiger are in accord with this idea, for he obtained derivatives having the general formula:



and which consequently are *ortho*-substituted acid azo dyes. Since the *para* position is occupied, *o*-hydroxyazo derivatives are formed, but the *ortho* position exists only in one benzene nucleus rather than in both nuclei, unquestionably because of steric hindrance. Other compounds can be prepared by combination with the diazonium derivatives of aniline, *p*-nitroaniline, sulfanilic acid, naphthionic acid, and benzidine. If the diazonium salt contains a sulfonic group, the resulting derivative is soluble in water. Analyses of these products agree fairly well, though not strictly, with the theoretical values.

In these experiments of Geiger,[5] there were obtained for the first time a new group of azo derivatives with very large molecules containing a great number of azo groups. But there is no possibility of obtaining by this method a complete series of azo dyes of widely different types. As may be seen from the general formula already shown, it is possible to form only acid dyes, and in turn, only those which contain substituents in *ortho* position. Accordingly, the number of dyes which can be obtained is extremely limited, and as a result the work of Geiger has passed almost unnoticed.

On the other hand, if the contrary procedure is followed, *i. e.*, if efforts are directed to obtaining an amine derivative of rubber by diazotizing the latter and combining the resulting diazonium salt with amines and phenols, it should be possible to obtain every imaginable dye whose molecule is derived from rubber. This is the procedure which has been followed in the present work and which will now be described.

In the works which have been mentioned, the reactions between rubber bromide and aromatic hydroxy derivatives were studied. In none of these works, however, was the possibility of a reaction between rubber bromide and other aromatic derivatives investigated. Now if it is desired to extend the Friedel and Crafts reaction to rubber bromide, it is not sufficient to prove that it reacts with phenols but it must also be shown that it will react with aromatic amines and likewise with aromatic hydrocarbons.

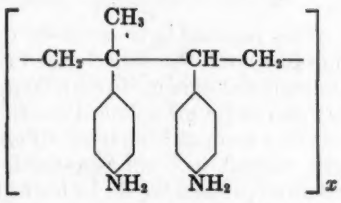
Accordingly it seemed of interest first of all to ascertain whether the bromide of rubber will react with benzene itself. This reaction, which does not take place simply by mixing rubber bromide and benzene, even at elevated temperatures, takes place on the other hand when a suitable catalyst is present. For example, if anhydrous ferric chloride is also present, there is a tumultuous evolution of hydrogen bromide, and the mixture turns brown. The details of the experiments which led to the formation of the product, which is unquestionably diphenylhydrorubber, will be described in a forthcoming communication.

To learn in the first place whether the reaction with aromatic amines is analogous to that with phenols, the reaction between rubber bromide and aniline was studied. The particular experimental procedure was as follows. Two grams of rubber bromide, 15 grams of aniline, and 0.5 gram of ferric chloride were heated for 6 hours, the temperature being raised gradually from 90° to 150° C. After cooling, 8 grams of sodium hydroxide were added, the excess aniline was eliminated by steam-distillation, the product was filtered, was washed with slightly acidified water, and, as a means of purification, was dissolved in acetone and then reprecipitated by addition of water. In this way there was obtained a dark brown or almost black powder, which was soluble in acetone, glacial acetic acid, and concentrated sulfuric acid, but was insoluble in these same acids in dilute form and in hydrochloric acid.

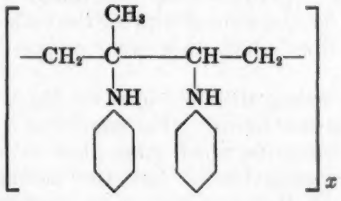
If the reaction were analogous to that with phenol, or better still, if it were of the Friedel and Crafts type, then there would have been obtained a compound analo-

gous to dihydroxydiphenylhydrorubber, *i. e.*, diaminodiphenylhydrorubber, and this product would have been soluble in the acids mentioned, by analogy with the phenolic derivative, which is soluble in alkalies.

This compound would have the following constitution:

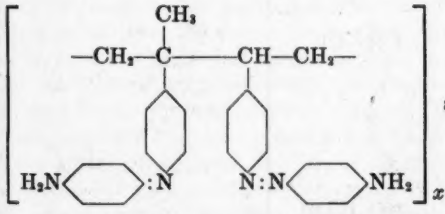


However, its insolubility in acids leads one to suspect that the reaction between aniline and rubber bromide takes place through the intermediary of the amine group, *i. e.*, a secondary amine of the following constitution is formed:



Nevertheless, the mere fact that the final product is insoluble in acids is not in itself proof of the absence of free NH_2 groups, and consequently it seemed of interest to study another reaction which might settle this point.

If the product of the reaction of rubber bromide and aniline contains free NH_2 groups, it should be possible to diazotize these groups and thus form diazonium salts which in turn should, when mixed with amines or phenols, form azo dyes of the general constitution



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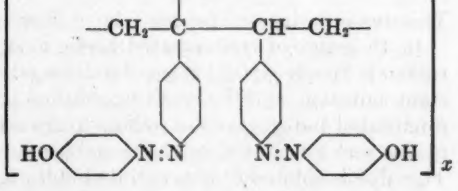


for basic dyes and acid dyes, respectively.

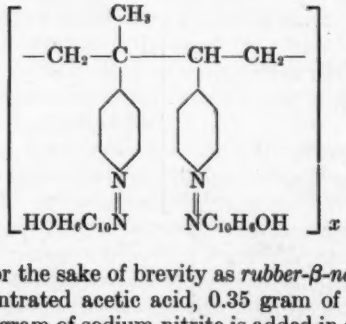
The experiments carried out in the present work have given positive results in that it was found possible to transform a part of the reaction product of rubber bromide and aniline into azo dyes. On the other hand, analysis of the derivative of rubber and aniline gave values which were so different from the theoretical value that they could not be attributed to experimental error or to impurities in the product.

In view of all this, it seems reasonable to conclude that the reaction between rubber bromide and aniline does not follow strictly the Friedel and Crafts reaction, but that only a part of the expected diaminodiphenylhydrorubber is formed, while at the same time secondary and as yet unexplained reactions take place, with probable formation of products of a resinous character. Perhaps, however, if the experimental conditions were changed, it might be possible that the reaction would proceed so that only the desired product would be formed.

In any event, it can be assumed that in the reaction of rubber bromide and aniline, diaminodiphenylhydrorubber is formed. This is the compound which can be diazotized, with formation of the dibenzenediazonium hydrorubber salt, which in turn couples with all known phenols and amines to form the most varied types of azo dyes derived from rubber. Analyses of all these products gave values which were, as was to be expected, in poor agreement with the theoretical values, since the diaminodiphenylhydrorubber from which they were prepared was of indefinite composition.

This reaction offers a means therefore of obtaining all the dyes derived from rubber which may possibly be desired. The number of dyes is still greater when it is realized that the same reaction which takes place with aniline also takes place with toluidine, xylidine, naphthylamine, and other aromatic amines. Like diaminodiphenylhydrorubber, all the products can be diazotized, and the diazonium derivatives react with amines and phenols. It is thus readily understood why the number of azo dyes derived from rubber which can be prepared in this way is practically unlimited. Among these are to be found dyes of the most varied tints and properties, which thus open vast fields of application.

As an example, the procedure followed in obtaining the dye from diaminodiphenylhydrorubber and β-naphthol may be described. This dye has a constitution which can be represented as follows:



This dye is designated for the sake of brevity as *rubber-β-naphthol orange*.

In 15 grams of concentrated acetic acid, 0.35 gram of diaminodiphenylhydrorubber is dissolved, 0.21 gram of sodium nitrite is added in small portions with constant agitation, and the resulting solution is poured into a solution of 0.42 gram of β-naphthol and 10 grams of sodium hydroxide in 50 cc. of water. There is obtained in this way a beautiful brick-colored product, which is filtered, washed, and dried. This dye is soluble in concentrated sulfuric acid, the solution having a beautiful rose color.

If, instead of mixing the diazonium salt with the alkaline solution of β-naphthol, it is mixed with a solution of aniline acetate, a solution is obtained which, when neutralized by sodium hydroxide, precipitates a brownish yellow dye. Then again when the diazonium salt is mixed with an alkaline solution of aminonaphtholdisulfonic acid, a beautiful bluish violet dye is obtained, which is only slightly soluble in water and which is colloidal.

These examples show that the widest variety of color tones can be obtained by combining diaminodiphenylhydrorubber or its homologs and diazonium derivatives with amines and phenols. There is thus opened a vast field of research which, it is to be hoped, will lead to practical results.

Unquestionably, these dyes, which are of high molecular weight and contain a large number of azo groups in their molecules, will have properties different from those of other azo dyes. Perhaps these properties can be utilized successfully in various practical ways, as in the rubber industry itself. In this respect a wide field remains open for experimentation.

Finally, it was of interest to ascertain whether the bromide of rubber used in preparing diaminodiphenylhydrorubber could be replaced by chlorinated rubber. From a theoretical point of view this may be of little interest since, as is known, the composition of chlorinated rubber does not correspond to the theoretical formula $(C_5H_8Cl)_x$. However, from a technical standpoint, it seemed of interest to see whether rubber bromide, the preparation of which is so uncertain and so expensive, can be replaced by chlorinated rubber, the preparation of which is simple and cheap. In the problem in question, it is of little importance whether each individual molecule contains exactly two atoms of chlorine or a greater number. Each chlorine atom should be replaced by a phenylamine radical without variation in the composition of the product obtained.

With this end in view, one gram of Tornesit was heated with 15 grams of aniline and 0.3 gram of ferric chloride, the same procedure being followed otherwise as in the case of rubber bromide. The reaction follows a similar course, and the product is identical, in so far as its appearance and properties are concerned, to that obtained by the reaction of rubber bromide and aniline. Analysis of this new product gave a somewhat higher nitrogen content, although in this case too it was different from the theoretical composition. As in the previous case, the product could be diazotized and combined in the same way as the product already described.

In summarizing the various facts which have been described up to this point, it can be said first of all that rubber bromide and likewise chlorinated rubber, which is the more important technically, react with aniline and other aromatic amines in the presence of ferric chloride as catalyst. After having separated the excess of amine, there is obtained a product of ill-defined composition, which, in the opinion of the author, is composed chiefly of diaminodiphenylhydrorubber in the case of aniline, and of its homologs or derivatives in other cases, despite the fact that these compounds do not dissolve in acids. These products can be diazotized in acetic acid or sulfuric acid solution by solid sodium nitrite or by an organic nitrite, and the resulting diazonium salts can be combined with amines and with phenols, and azo dyes derived from rubber can thus be obtained. The number of such dyes is very large, as is quite evident when one considers the great number of amines and of phenols which can combine with the diazonium derivatives. The azo dyes from rubber include the same groups as ordinary azo dyes. If a sulfonic group is present in the molecule, the dye is soluble in water. These dyes show all possible varieties of color. They are of high molecular weights, and each molecule contains a very large number of azo groups. In view of these peculiar properties, it is hoped that the new dyes will find extensive applications in various industries.

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Oxidation Products of Rubber: Rubbone

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The oxidation products of rubber have received considerable attention, both from the academic and technological points of view.[1,2] The present account deals with subsequent work on the oxidation product, termed Rubbone, and its derivatives.

Nature of Rubbone

Shortly, Rubbone is a viscous gum, yellow to orange-red in color, containing oxygen, corresponding approximately to $C_{10}H_{16}O$. The material obtained on a commercial scale consists of three fractions described as *A*, *B*, and *C*. These are distinguishable by their solubilities, as follows: *A*, soluble in white spirit and aromatic hydrocarbons, insoluble in acetone and alcohol; *B*, soluble in white spirit and aromatic hydrocarbons and acetone, insoluble in alcohol; *C*, soluble in acetone, aromatic hydrocarbons, and alcohol, insoluble in white spirit.

The commercial product consists mainly of fraction *B*, with very little of fraction *A*, and 10–20 per cent of fraction *C*.

If this is distilled to a temperature of 350°, a certain amount of destructive distillation takes place. Some dipentene is formed, which is not unexpected. A fraction between 200° and 300°, however, was found to contain polyhydric phenols. The amount of these was not large, being of the order of 1 per cent on the original Rubbone, but their presence is of interest. The washed neutral oils closely resemble rosin oil, formed by the destructive distillation of rosin. The amount of destructive distillation is not great, and the bulk of the Rubbone (80 per cent) remains as a still tacky gum, rather dark in color, above 350°.

Methods of Preparation

The method previously described,[3] namely by blowing air through a 20-per cent solution of rubber in white spirit in the presence of cobalt linoleate, has been developed to a semi-commercial scale, and several hundredweights of Rubbone have been produced. The commercial product probably contains a small quantity of high-boiling petroleum residues, which act as plasticizers and are useful rather than detrimental, but offer difficulties if it is desired to remove them to ascertain the properties of the purified products.

A more concentrated solution can be employed if the aeration is conducted under pressure, thus reducing the loss of solvent by volatilization in the exhaust gases.[4] An alternative method of circulating oxygen under pressure is not recommended. The reaction is exothermic and is not easily controlled.

A third method of manufacture has been evolved which has proved to be of considerable interest from both the commercial and theoretical points of view, as it dispenses with the use of a solvent and consequently yields products free from any petroleum residues.

Since the process consists essentially in adding oxygen to catalyzed rubber, that is, rubber into which a catalyst has been milled, it seemed likely that the oxidation could be effected by disposing the rubber in a thin film and exposing it to the action of air at a reaction temperature of, say, 75–80° C. This was accomplished by adding to the catalyzed rubber on the mill a powdered material offering a large surface. The resultant product was then extracted with a suitable solvent or used directly in the powder form for certain applications—molding powders, for example.

Experiments were tried with various media, and a somewhat unexpected reaction was discovered. With such materials as kieselguhr, slate dust, powdered asbestos, etc., the amount of oxidation even with prolonged milling was comparatively low. It rarely amounted to 10 per cent of the possible conversion into Rubbone.

With cellulosic materials such as wood flour, wood pulp, paper, cotton wool, etc., the reaction was so rapid that frequently the material charred, with evolution of strong aldehydic and acid fumes. Leather dressings and wool behaved similarly. At first it was thought that this reaction was purely a surface phenomena, but carefully measured experiments demonstrated conclusively that some reaction was taking place in which the cellulose was playing an important part, possibly acting as a second catalyst. The catalytic oxidation of cellulose with cobalt linoleate was also confirmed. The reaction varies proportionally to the quantity of cellulose present, and for a given amount is greatest with cotton and least with wood flour. It has been found that the addition of a small quantity of fine neutral and inert material or fillers, such as whiting, amounting to no more than 15 per cent, accelerates the action considerably. Apparently, such fillers function as grinding media for the cellulosic material, thereby offering the necessary surface in the minimum of time. The whole reaction is begun and completed on hot rolls as ordinarily used in rubber milling.[5]

The following tables illustrate some of the results obtained by the "dry" method. Figures are calculated on the amount of "catalyzed rubber" taken. Twenty per cent of kieselguhr was used in each case.

TABLE I

Source of Cellulose	Per Cent Taken	Per Cent Conversion Measured by Acetone Extract
Cotton	50	30
Cotton	65	80
Chemical wood pulp	30	5.6
Chemical wood pulp	40	5.0
Chemical wood pulp	50	7.5
Chemical wood pulp	60	27.0
Chemical wood pulp	70	62.5
Chemical wood pulp	75	64.0
Chemical wood pulp	80	76.0
Chemical wood pulp	85	77.0
Wood flour	100	3.0
Wood flour	150	13.0
Wood flour	200	90.0

Basing the figures on the above table, the efficiencies of the three catalysts, putting wood flour = 100, are approximately as follows: wood flour 100, wood pulp 250, cotton 325.

Mixtures were made from cotton and wood flour to give a cellulose content of approximately 66 per cent. The following results were obtained:

Cotton	Wood Flour	Per Cent Conversion Measured by Acetone Extract
40	80	22
34	100	36.5
28	120	48.5
20	140	59.0
14	160	71.0
7	180	82.0
Nil	200	80.0

The increase is practically a linear function of the content of wood flour, which presumably offers the surface required.

An 80-per cent conversion can be obtained from 65 parts of cotton and 20 parts of kieselguhr, from which it may be inferred that the surface effect of kieselguhr in conjunction with cotton is considerably better than that of wood flour.

The product is a soft, powdery material which becomes hard on cooling. It is readily extracted with solvents so that it can be used as a source of Rubbone, or any Rubbone fraction it may be desired to produce. Material thus prepared can be used as the basis for the manufacture of other derivatives, such as the hydrochloride, chlorinated compounds, or vulcanized compounds. Also for the preparation of these derivatives the reaction mixture can be used without previous extraction (see later under "Chlorine derivatives").

Properties of Rubbone

The principal properties, previously described,[2] may be summarized briefly. When heated out of contact with air, Rubbone slowly polymerizes until it acquires the form of a tough, non-tacky gel similar to polymerized wood oil. When heated in contact with air, further oxidation takes place and the material becomes hard and brittle. In this condition it is not of much value. It is, however, readily miscible with drying oils, which act as plasticizers for it. The drying oils retard polymerization. On the other hand, Rubbone accelerates the oxidation of polymerized linseed oil. It is thus possible to formulate a baking varnish suitable for the lacquer industry and for the electrical industry by simply adding stand oil to a solution of Rubbone in solvent naphtha. The tedious and somewhat costly method of gum running is thus avoided. The film produced by the oxidation of such a mixture is extremely flexible and tough. It adheres well to metals such as iron, tin, aluminium, and zinc but not so well to copper. It is also resistant to organic acids normally associated with fruit juices and therefore suitable for lacquering tins as indicated below.

Polymerization.—The polymerization of Rubbone measured in terms of increased viscosity is shown in Fig. 1, in which viscosity has been plotted against time. The inhibiting effect of stand oil is also shown.

Certain agents accelerate polymerization, of which the following are a selection: oxalic acid which gives a very marked result; also benzoyl peroxide, phosphoric acid, succinic acid, cinnamic acid, tannic acid, phthalic anhydride, toluidine.

Resistance of Films to Weak Acids.—It has been shown[6] that when citric, tartaric, or acetic acids act on a piece of tinned sheet the rate of attack can be ascertained by the amount of iron found in solution. This method was applied to tin sheet lacquered with rubber varnishes with the following results. The varnishes employed were made by dissolving rubber (40 parts) milled with 2.5 per cent of cobalt linoleate in white spirit and 60 parts of either stand oil or raw linseed oil. These were broken down with white spirit in the proportion of 25 per cent by weight of

above base and 75 per cent by weight white spirit. Ordinary fruit tins were cleaned and lacquered with two coats of the varnishes and baked for 1.5 hours at 155°. During the baking the rubber is converted into Rubbone and forms a hard, resistant film in conjunction with the oil. The solution used for corrosion tests was 0.5-per cent citric acid, with a p_H value of 2.4. This has been found to give the maximum corrosion. Two sets of tests were made over prolonged periods, one cold and another an accelerated test at 70°. The course of corrosion was noted by a color test. By taking a small quantity of the citric acid under test, diluting, and adding ferrocyanide, the color could be matched against standard Prussian-blue suspensions and an approximate estimation of the corrosion determined. The results given below are expressed as grams of iron per 1000 sq. cm. of surface.

Period in Days	Stand Oil	Linseed Oil
	Cold Test	
9	0.20	0.005
13	0.42	0.07
52	0.45	0.27
	Hot Test at 70°	
1	0.03	0.02
3	0.20	0.20
6	0.25	0.30

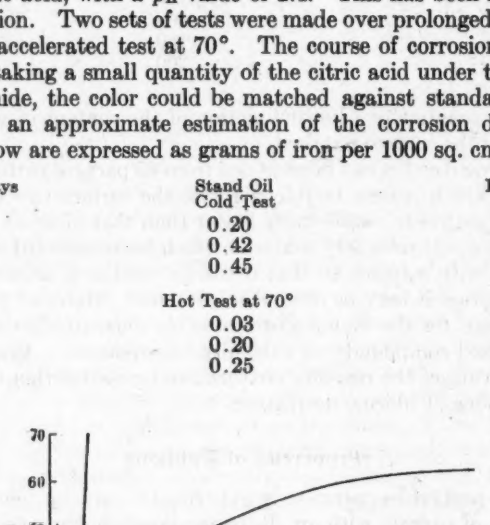

Figure 1—Viscosity of Rubbone-Linseed Oil Mixtures

After 6 days (when the films were rather soft) the samples were tested for tin, with the following results: stand oil film 0.005 per cent; linseed oil film 0.015 per cent (the amount of tin permissible in food is 0.03 per cent).

A further set of tins were similarly lacquered but were heated at 120° for 18 hours. After baking in order to mature the film, and when tested by the accelerated test, they showed similar amounts of corrosion as far as dissolution of iron was concerned, but tin was absent.

Several tins lacquered by other processes which had contained strawberries, peas, raspberries, and red currants were treated with citric acid by means of the above described test. The amounts of iron dissolved after 6 days were 1.08, 0.27, and 1.8 g., respectively; tin was present in traces only. The Rubbone varnish would therefore appear to be quite comparable with the ordinary commercial lacquers used for this purpose.

Electrical Tests.—A detailed account of the electrical properties of Rubbone has already been published.[7] The main properties are as follows: breakdown voltage, 57–76 kv.; dielectric test on paper samples: 1 mil tissue paper, 625 volts per mil; 5 mil pressboard, 785 volts per mil; specific resistance, tested at 70° after 3 hours at 110°, 2.2×10^9; tested at 20° on cooling, 2.8×10^{11}; tested at 70° after 50 hours at 120° in contact with copper, 1.0×10^{10}.

Considerable improvements were effected by applying Rubbone in the form of baked varnishes. For this purpose, mixtures with stand oil were made in a manner similar to those used for baking lacquers.

The outstanding properties of the material in their relation to its electrical applications would appear to reside in the high moisture-resisting properties of the baked film and in the increased strength given to asbestos millboard when treated and baked with Rubbone mixtures.

Vulcanization of Rubbone

Rubbone readily reacts with sulfur in a manner similar to raw rubber to form vulcanized products. Those corresponding with low and medium combined sulfur are of no particular interest, but as the percentage of sulfur approaches that of hard rubbers some interesting products are formed. In the first place hardening is very rapid, two hours at 100° with 10 per cent of sulfur being sufficient to produce a product which is hard and brittle when cold although retaining some thermoplastic properties. The hardening may be caused partly by vulcanization and partly by the heat-hardening properties of the resin. A detailed study of the vulcanization and properties of Rubbone will be published later.

The technical interest also lies in the possibility of making molding powders. For this purpose a Rubbone-paper mix can be utilized, with or without added filler. There is no need to extract the Rubbone. In fact the operation can be continued from the preparation of the reactive mixture without removing the material from the rolls. It is only necessary to add the sulfur, etc., mill sheet, and complete the vulcanization for a few hours at 100°, finally grinding in order to obtain a thermoplastic molding powder. It is also possible to obtain such a powder without the addition of the sulfur, but moldings from these powders lack strength. The chief value of these molded products lies in their excellent anti-tracking properties. It has also been found that if the vulcanizable sheet, prepared as above, be softened with rosin oil and thinned with solvent naphtha an excellent cement is obtained for cementing rubber to metal.

Another possible application of the material is to be found in the formation of a vulcanizable cement for emery and carborundum wheels, and some success has been obtained in this direction. The quality of the vulcanizable cement depends in part on the reinforcing character of fillers. With Rubbone cements the effects produced by the filler do not necessarily follow the same order as in the case of rubber. The following results indicate some of the differences. Cements were made ac-

	Cement				Filler			
	Rubbone	Sulfur	Zinc Oxide	China Clay	Litharge	Silica 300-Mesh	Breaking Load Kg. per Sq. m.	Breaking Strain Elongation
(1)	100	100	40.0	..	..	..	0.52	5.0
(2)	100	10	5.0	35	..	..	0.27	5.0
(3)	100	15[a]	5.0	..	35	..	0.43	5.0
(4)	100	10	5.0	..	..	35	1.22	7.5

[a] 5 grams of this sulfur were intended to allow for the sulfur retained in combination with the litharge.

cording to the preceding table. The mixtures were thickened by heating at 100°. After thickening they were milled with 3 parts by weight of silica (300-mesh) and sheeted. Dumbbell-shaped test-pieces were cut from the sheet, vulcanized at 110° for 24 hours, and tested between grips in a Schopper machine.

The pronounced reinforcing action of silica was unexpected and has since been confirmed.

It is obviously advantageous from the commercial point of view to form a cement from the Rubbone-paper mix obtained in the course of manufacture. Samples of these were vulcanized and tensile tests were made. The results appeared to depend to some extent on the sulfur content as well as on the varying proportion of the different Rubbones present. For example, a mixture containing only 5 per cent of sulfur calculated on the Rubbone showed a tensile strength of 1.78 kg. per sq. mm. compared with 0.92 kg. for the same material compounded with 10 per cent of sulfur. Other samples consisting of Rubbone *A* and of Rubbone *A* plus unconverted rubber showed tensile strengths varying from 0.16 to 0.47 kg. Vulcanized products containing zinc oxide or magnesium oxide were unexpectedly weak.

Chlorine Derivatives

Hydrochloride.—In common with other substances of a similar build, both rubber and Rubbone form additive compounds with hydrochloric acid. The Rubbone product is readily prepared by passing dry hydrogen chloride gas into a cooled solution of Rubbone in xylene. The hydrochloride is not readily soluble in white spirit and the solution soon gels much in the same way as a rubber sol to which a small proportion of sulfur chloride has been added. It is not possible to add molecular quantities of acid without the liquid gelling, and the partly saturated material gels after setting aside for a time. A film obtained by rapid evaporation possesses excellent alkali-resisting properties and, but for the tendency to gel, would probably find a useful application in this direction. One rather remarkable property is its capacity for allowing alkali to pass through without being itself affected and without the alkali affecting pigment suspended in it. Thus, for instance, if Prussian-blue be incorporated with the solution to form a paint and this be applied to fresh concrete kept moist by standing in a tray of water, the soluble alkali from the concrete penetrates the layer of Prussian-blue paint without discharging the color of the latter. That penetration has taken place is indicated by the discharge of the color of an ordinary Prussian-blue paint in an oil medium painted on the surface of the original layer. Thus if gelling could be prevented, the material could be made useful as a "breathing" alkali-resistant coat for plaster or concrete.

A method of gel prevention has been found by the incorporation of coumarone resin in the solution. This resin can be added before or after chlorination. Excess, that is, more than 50 per cent, will form a sealing medium and not a breathing one. It is possible to add as much as twice the quantity of Rubbone and still obtain a "breathing" medium in spite of the sealing action of coumarone when used alone.

The phenomenon just mentioned does not appear to be one admitting of a simple explanation. Clearly the film is of a permeable or semipermeable kind in those cases where "breathing" is experienced. Nevertheless, the pigment particles dispersed in the film are protected as shown by the fact that the color is not discharged. There is some evidence that the concentration of alkali has some effect on the result. In one experiment, for example, carried out on cardboard and not concrete the product acted as a "breather" to 5-per cent and 10-per cent caustic

soda solution and as a "sealer" to a 2.5-per cent solution. There is thus a possibility that a different behavior may be experienced with different concrete and even with different parts of a single block of concrete.

It is possible to manufacture the hydrochloride direct from a Rubbone-paper mix prepared as already described for the manufacture of Rubbone. If this is crumbed and mixed in a ball mill with the requisite quantity of concentrated hydrochloric acid and then air-dried, the Rubbone hydrochloride can be extracted quite readily. The material prepared in this way does not gel quite so rapidly as that prepared by passing the dry gas through the solution but it forms a weak gel in time.

Chlorinated Rubbone.—If dry chlorine is passed through a cooled solution of Rubbone in an inert medium such as a chlorinated hydrocarbon some substitution takes place with the evolution of hydrogen chloride. This offers some evidence that the molecule is cyclized and no longer in the form of a long chain. The product is a tacky gum, very different therefore from chlorinated rubber, and dries when pigmented with a glossy finish.

A product may be prepared by milling the above-mentioned Rubbone-paper mix with or without fillers, with a halogen carrier such as bleaching powder. This behaves in a similar manner to that prepared by direct chlorination of Rubbone, but it is not yet known whether the two products are identical. The formation of a hypochlorite is possible and is being further investigated. It has not been found possible to chlorinate Rubbone by this method to the same degree as by direct chlorination. The degree of chlorination has been found to be of some importance and also the particular resin chlorinated. If the chlorine content is below 50 per cent, full pigment protection is not obtained, although the film acts as a "breather."

For this reason the method of manufacture utilizing bleaching powder is not very attractive, since the highest degree of chlorination so far obtained in this way is only 12 per cent. The three resins differ as follows: Rubbone *A* chlorinated to above 50 per cent acts as a "breather" even when mixed with coumarone resin; Rubbone *B* chlorinated to a similar extent acts as a "sealer," and Rubbone *C* also acts as a "sealer," but is not so effective as a pigment protector. It is interesting to note that the chlorinated Rubbone *C* gives solutions of lower viscosity than solutions of the same concentration of the other resins. The influence of this on pigment protection in relation to brushing out and irregularities of surface may be of importance.

The chlorination products of Rubbone are much more stable than the hydrochloride. The tacky film formed by evaporation can be rendered free from tack by incorporating pigments and mixing with chlorinated rubber or coumarone, with which it is compatible. Films formed by this combination are bright and clear, somewhat brittle, resistant to alkali and to abrasion.

Chlorination may conveniently be applied to mixtures of Rubbone and coumarone in solvent naphtha. Chlorination of the solvent takes place simultaneously but to a rather less degree, as shown by tests in which a solution of 25 per cent of Rubbone in solvent naphtha was added to an equal part of a 50-per cent solution of coumarone in the same solvent, with the following results:

Chlorine on Separated Gum, Per Cent	Chlorine in Solvent, Per Cent	Ratio
14.7	6.8	2.2
24.5	11.3	2.2
40.5	29.7	1.4
44.2	29.4	1.5

The chlorination of the solvent was probably approaching completion at about 30 per cent under the conditions prevailing.

Summary

(1) The methods of making Rubbone are described and data given regarding the "dry" method in which rubber containing catalyst is milled with cellulosic materials and fillers.

(2) The properties of Rubbone are described, including the polymerized products, the resistance of films to weak acids as for lacquering tins, and the electrical properties.

(3) Rubbone can be vulcanized with sulfur. The products have applications as cements.

(4) The method of preparation and properties of the hydrochloride and chlorinated Rubbone, and their use as a basis for alkali-resistant paints are described. These products have a tendency to gel, but this may be prevented by the incorporation of coumarone.

This work has been carried out on behalf of the Rubber Producers Research Association, to whom the authors are indebted for permission to publish.

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[Translated for Rubber Chemistry and Technology by K. Kitsuta from the Journal of the Society of Rubber Industry of Japan, Vol. 10, pages 273–277, 431–434 (1937).]

Studies of Organic Accelerators

XVI. Part 4. Detection and Analysis of Organic Accelerators. Detection of Guanidine Accelerators in Vulcanized Rubber

Keichi Shimada

Organic vulcanization accelerators are essential for vulcanizing rubber, and their detection and analysis are becoming more important to rubber technologists.

Methods of analysis of accelerators are, however, not practical at present; moreover, in its present state of development, quantitative analysis gives only approximate results, because accelerators undergo fundamental chemical changes at vulcanizing temperatures.

For this last reason, it is difficult even to test for organic accelerators qualitatively, and many of them cannot be identified.

The difficulty of detecting organic accelerators in vulcanized rubber is due mainly to their complicated chemical properties and their low percentages; moreover, many organic accelerators change their chemical structure and some disappear entirely during vulcanization.

Although the number of organic vulcanization accelerators in the literature is great, the different types which are used in rubber factories are much fewer. By classifying organic accelerators according to their efficiency of acceleration into weak, medium, semi-super, and super accelerators, it will be found that only a few in each class are used in practice. Accordingly, there is a limited number to be detected in technical work. This is the general situation at present, but it is hard to tell how many more accelerators will be used in the future; so any methods of detection which are developed should be applicable to other organic accelerators.

The author has already developed a systemic method of detection of various commercial accelerators based on color reactions of cobalt oleate (cf. *J. Soc. Rubber Ind. Japan*, **6**, 263 (1933)). This method has now been applied to vulcanized rubber in an attempt to detect organic accelerators. Some organic accelerators are believed to be permanent, whereas others supposedly disappear or change during vulcanization. There is, however, no experimental proof of this.

Since the problem was to develop a systemic method of detection of organic accelerators in vulcanized rubber, the first experiments were concerned with the detection of guanidine, thiazole, and thiocarbamate accelerators, which are those most commonly used by the rubber industry.

This report deals with guanidine accelerators.

EXPERIMENTAL

1. Preparation of Sample

Diphenylguanidine, di-*o*-tolylguanidine, and *o*-tolylbiguanide, which are the most commonly used guanidines, were chosen as representative of this group. They were purified from the commercial accelerators by recrystallizing three times from benzene. The mixtures were of the following composition:

Pale crepe	100
Sulfur	3
Zinc oxide	3
Stearic acid	1
Accelerator	1

The mixes were prepared on a laboratory roll at 50° C., and vulcanized in a press at 148° C. for 15, 45, 60, and 90 min. The samples were cut into small pieces for testing.

The reagent was cobalt oleate in benzene (cf. *J. Soc. Rubber Ind. Japan*, **6**, 268 (1933)).

2. Method of Detection of Organic Accelerators

Accelerators of this type dissolve readily in alcohol and in acetone. Accordingly, if part of a guanidine accelerator remains unchanged in vulcanized rubber, it can be extracted by alcohol or acetone. Acetone is recommended.

One difficulty, however, in using a benzene solution of cobalt oleate is that it gives a white precipitate when it is added to acetone. Although addition of cobalt oleate solution to acetone containing a guanidine accelerator gives a characteristic coloration, the color becomes obscure because of this white precipitate. More than 100 parts of solvent containing 20 parts acetone and 80 parts benzene or more than 100 parts containing 10 parts alcohol and 90 parts benzene are required for solution of cobalt oleate.

For this reason, the present author has used acetone as a solvent for extracting accelerators in the same way as in the acetone extraction of vulcanized rubber. The accelerators are then recovered by suitable methods from the residue after evaporation of the acetone.

There are several methods of extracting accelerators from the acetone extract. The simplest way is to treat the acetone extract with benzene, but the result of this method is not so good, as it dissolves resins and sulfur at the same time, and the benzene solution is so dark brown that the coloration is obscured to a considerable extent. Decolorization of the benzene solution with acid clay or bone charcoal is unsatisfactory. In general, then, extraction of the acetone extract by benzene is unsuitable.

The second method is to extract the acetone extract with alcohol, dissolve the residue in benzene, and test for a color reaction with cobalt oleate. This procedure removes the color of the extract to a considerable extent in comparison with the first method, but it is still unsatisfactory, especially when the content of accelerator is small.

A third method is to extract as sulfate by treating the acetone extract with dilute sulfuric acid, since guanidine accelerators are bases. They are then transformed into the original accelerators by treating them with dilute alkali and extracting with benzene after evaporation to dryness. The color test of this benzene extract is satisfactory.

Procedure.—Extract 10 grams of vulcanized rubber with acetone for 8 hours, evaporate to dryness, dry in air at 70° C., add 20–30 cc. 0.1 *N* sulfuric acid, heat on a water bath for 30 min., filter, neutralize the filtrate with 0.1 *N* sodium hydroxide, evaporate to dryness, add 10–15 cc. of benzene to the residue, warm gently, filter, cool, and add cobalt oleate. The benzene solution of cobalt oleate turns green, then purple on heating, but it regains its original color on cooling as with many complex cobalt salts; therefore, the color reaction must be noted on cold solution.

3. Experimental Results

With this method, vulcanized rubbers containing various guanidine accelerators were tested. The results follow:

Sample No.	Accelerator	Time of Vulcanization (Minutes)	Color Reaction
1	Diphenylguanidine	90	Slightly purple
2	Di-*o*-tolylguanidine	90	Slightly purple
3	Di-*o*-tolylbiguanide	90	Slightly pink
4	Diphenylguanidine	60	Slightly purple
5	Di-*o*-tolylguanidine	60	Light red-purple
6	*o*-Tolylbiguanide	60	Light brown-red
7	Diphenylguanidine	45	Purple
8	Di-*o*-tolylguanidine	45	Deep purple
9	*o*-Tolylbiguanide	45	Light pink
10	Diphenylguanidine	15	Purple
11	Di-*o*-tolylguanidine	15	Deep purple
12	*o*-Tolylbiguanide	15	Pink

These results indicate that guanidine accelerators in vulcanized rubber can be detected satisfactorily by cobalt oleate. Samples vulcanized for relatively long times showed rather feeble colorations, probably because the guanidine accelerators changed into other compounds during vulcanization.

SUMMARY

The experiments were planned with the hope of detecting various organic accelerators in vulcanized rubber. The present report deals with three important guanidine accelerators in vulcanized rubber. The detection of organic accelerators by the use of cobalt oleate has already been described, and the present work describes the method of extraction of guanidine accelerators from vulcanized rubber and the procedure used for their detection. The results indicate that the method is satisfactory.

XVIII. Part 6. Detection of Dithiocarbamate Accelerators in Vulcanized Rubber

Although perhaps fifteen or more dithiocarbamate accelerators have been developed for the rubber industry, only a few of these are commonly used. The author has already studied the color reactions of thirteen of these with cobalt oleate reagent, and has found that all give positive reactions.

With the hope of applying this method to the detection of this type of accelerator in vulcanized rubber, the author tested three representative accelerators, piperidinium pentamethylenedithiocarbamate, zinc ethylphenyldithiocarbamate, and cyclohexylethylamine cyclohexylethyldithiocarbamate. The results were as expected, and they gave valuable information in explaining the mechanism of acceleration of dithiocarbamate accelerators. This report deals mainly with the method of detection and the results.

EXPERIMENTAL PART

Vulkacit P for piperidinium pentamethylenedithiocarbamate, Vulkacit P Extra for zinc ethylphenyldithiocarbamate, and Vulkacit 774 for cyclohexyl ethylamine-

dithiocarbamate were used for the tests. Each was recrystallized from benzene. The base mixture (by weight) was as follows:

Standard smoked sheet	100
Sulfur	2.5
Zinc oxide	5
Calcium carbonate	25
Stearic acid	1
Accelerator	0.5

The compounded rubber mixtures were vulcanized in a press at a steam pressure of 15 lb. per sq. in. for various times.

To detect a dithiocarbamate accelerator in vulcanized rubber, it must first be extracted. When a ground sample was extracted in boiling water for 30 min., the filtered solution dried on a water bath, and the residue taken up with benzene, the test with cobalt oleate was negative. This showed that aqueous extraction is unsuitable (needless to say it is unsuitable for water-insoluble salts); therefore recourse was had to acetone extraction as in the preceding work.

Five-gram samples of rubber vulcanized with piperidinium pentamethylenedithiocarbamate, zinc ethylphenyldithiocarbamate, and cyclohexylethylamine cyclohexylethyldithiocarbamate were cut into small particles and extracted for 5 hours with acetone. The residues after evaporation of acetone were dissolved in 10 cc. benzene, and the colorations with cobalt oleate were noted. All samples gave dirty yellowish green colorations, which made a positive test for the dithiocarbamate accelerators somewhat uncertain. The cause of this trouble will be described later, but since acetone extraction seemed unsuitable, benzene extraction was tried.

Five grams of finely ground sample were extracted for 2 hours with benzene, the extract was condensed to about 10 cc., and cobalt oleate reagent was added. In all cases a characteristic clear yellowish green coloration was observed. In this experiment, all samples containing each accelerator and vulcanized for periods from 5 to 80 min. gave positive reactions. It is thus clear that dithiocarbamate accelerators in vulcanized rubber can be easily detected by testing a benzene extract with cobalt oleate, provided that no substance in the rubber darkens the color of the extract.

Except for zinc ethylphenyldithiocarbamate, the accelerators are readily soluble in acetone and they should be extracted with acetone; nevertheless they were not extractable. This is probably attributable to the formation of acetone-insoluble zinc salts by reaction with zinc during vulcanization. This will be discussed elsewhere.

Test of the solubility of zinc salts in acetone formed by the reaction of aqueous piperidinium pentamethylenedithiocarbamate or cyclocyclohexylethylamine cyclohexylethyldithiocarbamate with zinc sulfate showed that they are difficultly soluble. Since they are fairly soluble in benzene and show a clear yellowish green color with cobalt oleate, it is preferable to use benzene as a solvent to extract these accelerators from vulcanized rubber.

SUMMARY

Tests of the possibility of detecting dithiocarbamate accelerators such as piperidinium pentamethylenedithiocarbamate, zinc ethylphenyldithiocarbamate, and cyclohexylethylamine cyclohexylethyldithiocarbamate in vulcanized rubber by the color reaction of the author's cobalt oleate reagent are described. In all cases, it gave a characteristic clear yellowish green coloration of dithiocarbamate. Ben-

zene, not acetone, is the best solvent for extracting dithiocarbamate accelerators from vulcanized rubber. An explanation of this is offered.

XIX. Part 7. Detection of Thiuram Accelerators in Vulcanized Rubber

Although tetramethylthiuram disulfide and tetramethylthiuram monosulfide do not give any color reactions with cobalt oleate, the color of tetramethylthiuram monosulfide itself is yellowish and different from the color of other organic accelerators. This color is useful for distinguishing it. It has already been shown by the author that tetramethylthiuram disulfide can be reduced to the corresponding thiocarbamate under suitable conditions, and the latter can be detected by its color reaction with cobalt oleate.

It was of interest to ascertain whether thiuram accelerators can be detected by the author's color reaction, since this would be important not only in analytical chemistry but in explaining the mechanism of acceleration.

EXPERIMENTAL

Preliminary tests were carried out to see whether tetramethylthiuram monosulfide or disulfide can be extracted easily.

Mixtures prepared from pale crepe 100, sulfur 3, zinc oxide 5, stearic acid 1, accelerator 1, were vulcanized at 135° C. for 20, 30, 40, and 60 min. Five-gram samples were ground and extracted with acetone, the acetone was removed, and the residue was dissolved in 10 cc. of benzene.

The benzene solutions from the samples containing tetramethylthiuram disulfide and vulcanized for 40 and 60 min. gave with cobalt oleate reagent a dirty yellowish green coloration of low intensity. Benzene solutions from the samples cured 20 and 30 min. were reduced with zinc dust and dilute sulfuric acid, and the benzene layers were tested with cobalt oleate. The coloration was more distinctly yellowish green.

A benzene solution from the sample containing tetramethylthiuram monosulfide should have given a characteristic yellow color of this accelerator, but benzene-soluble substances such as resins and free sulfur may also give yellow colors. Therefore, the color of the benzene extract is not reliable as a means of detection. However, addition of cobalt oleate reagent to benzene solutions of samples vulcanized for various times gave clear, light yellowish green colorations.

As already described, tetramethylthiuram monosulfide gives no color reaction with cobalt oleate and tetramethylthiuram disulfide gives a positive color test only after reduction. This is an interesting reaction, and the author believes that it gives an important clue to the mechanism of acceleration. This will be discussed elsewhere.

Since it was found that thiuram accelerators can be detected by their color reactions with cobalt oleate the following experiments were made: a mixture composed of smoked sheet 100, zinc oxide 5, accelerator 1, sulfur 3, stearic acid 1, calcium carbonate 25, was vulcanized in steam at 35 lb. per sq. in.

Since thiuram accelerators are easily soluble in acetone, acetone was chosen as a suitable solvent. Preliminary tests, however, indicated that these compounds change during vulcanization, probably into dithiocarbamates. Both acetone extraction and benzene extraction were therefore carried out.

A ten-gram sample containing tetramethylthiuram disulfide was extracted with acetone for 5 hrs., the extract was dried, and the residue was taken up with a little benzene. Benzene solutions from samples vulcanized for various times gave light reddish yellow colorations, but solutions from samples vulcanized for more than 20 min. gave only light yellow colorations, and no great difficulty was encountered in detecting the accelerator by its color reaction.

Benzene solutions from samples vulcanized for 5 to 50 min. were prepared and their coloration with cobalt oleate was noted. Though the colorations were light, all were yellowish green. These facts indicate that no further treatment, such as reduction with zinc and sulfuric acid, is necessary. Yet this color reaction is not due to tetramethylthiuram disulfide but to the dithiocarbamic acid salt. If so, the salt must be a zinc salt, and extraction of the accelerator with acetone, as described in Part 6 of this series, is disadvantageous.

Therefore, 5 grams of vulcanized sample were extracted with benzene for 2 hrs., the sulfur deposited after cooling was filtered, and the benzene was concentrated to 10 cc. Addition of cobalt oleate gave a far better and clearer yellowish green coloration compared with the color of the acetone extract.

This gives a clue to the mechanism of acceleration by tetramethylthiuram monosulfide. The author favors the theory of Bedford and Sebrell (cf. *Ind. Eng. Chem.*, **14**, 25 (1922)) that this accelerator is effective only after changing into a dithiocarbamate (mainly zinc salt). This will be discussed later in a report on the "mechanism of vulcanization acceleration of organic accelerators."

Samples vulcanized with tetramethylthiuram monosulfide were extracted with acetone in the same way as were those with tetramethylthiuram disulfide, and the residue from the acetone extract was dissolved in a little benzene. Cobalt oleate reagent gave a clear yellowish green coloration as in the preliminary experiment, though the intensity of color was rather weak.

Other samples of vulcanized rubber were extracted with benzene, filtered, and concentrated. Cobalt oleate gave still clearer yellowish green colorations. This reaction was obviously the same as that of dithiocarbamates, *i. e.*, tetramethylthiuram monosulfide changes to a thiocarbamate during vulcanization. This is very interesting as an experimental proof of the mechanism of acceleration.

In short, tetramethylthiuram monosulfide and disulfide do not exist in their original forms in vulcanized rubber, except, in the case of undercured rubber or rubber containing excessive accelerator, but change into the dithiocarbamate during vulcanization.

The author considers this to be a fact rather than a hypothesis; hence it is difficult to distinguish thiuram accelerators from dithiocarbamate accelerators, since thiuram accelerators are detected in vulcanized rubber as dithiocarbamates.

Thiuram compounds are a good example of accelerators which change into other compounds during vulcanization; however, it is possible to obtain a color reaction by taking up the residue from the acetone extract with benzene, reducing the benzene solution with zinc and sulfuric acid, and adding cobalt oleate. If there is any unchanged tetramethylthiuram disulfide, it will then give a characteristic reaction.

SUMMARY

Rubber vulcanized with a thiuram accelerator such as tetramethylthiuram monosulfide or disulfide was tested with the author's cobalt oleate reagent after extraction with acetone and solution of the residue from the acetone extract in benzene, by testing the benzene extract of such vulcanized rubber. In all cases a characteristic yellowish green coloration of dithiocarbamate was observed. From this it is con-

cluded that thiuram accelerators are transformed into dithiocarbamates during vulcanization. Accordingly, it is difficult to ascertain whether accelerators in vulcanized rubber were originally present as thiuram compounds, except when the rubber is undercured or when an excessive amount of accelerator is used. Here, too, the greater part is detected as dithiocarbamate. An experimental proof of the mechanism of acceleration is offered.

Thanks are due to S. Ohtaki for his aid in the experiments.

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Difficulties in the Thorough Impregnation of Textiles with Latex

J.-Ch. Bongrand

In a patent of 1920 by Hopkinson, there appears the claim that cotton thread need only be immersed in latex to bring about complete impregnation and even penetration of the latex into the canals of the fibers. This is a quite unwarranted claim, and it can be explained by the fact that Hopkinson was primarily a lawyer as far as patents are concerned, and there is a natural tendency in this profession to place a mortgage on future accomplishments.

As a matter of fact, in spite of its very low viscosity (200 times less than that of benzene solutions containing the same percentage of rubber), latex does not penetrate spontaneously into textiles in the same way that clear solutions of rubber do. The work of Hauser and Hünemörder (cf. RUBBER CHEM. AND TECH., 5, 685(1932)) has more or less settled this question. According to their technic, rubberized threads to be examined are immersed in gelatin, the preparation is frozen by carbon dioxide, and fine sections are cut by means of a microtome. The gelatin and also the cotton structure which has not been impregnated are then destroyed by concentrated sulfuric acid, and are eliminated by washing. The remaining rubber has a red-brown color. In this way Hauser and Hünemörder established definitely that whereas clear solutions containing, for example, five per cent of rubber, penetrate cotton threads, latex only coats them superficially and does not penetrate them.

Two years before this work of Hauser and Hünemörder, the present author undertook to develop a method of impregnating textiles with latex. After having proved the part played by the twist in the threads, resort was had to the assistance of a cotton expert. At the end of 1931 the products obtained were submitted to E. A. Hauser for him to examine by his own technic. This examination was quite conclusive. In submitting enlarged photographs of the microscopic pictures which he had obtained, he offered the following comments on the results.

Figure 1 represents a section of a single thread of Filastic after the thread had been treated according to the new method (*Filastic* is the term which has been chosen for the result attained by the impregnation process of the present author). In contrast to this, Fig. 2 represents a section of a thread treated with latex by ordinary methods. The difference lies in the fact that the thread shown in Fig. 2 has been carbonized and dissolved by treatment with sulfuric acid so that only the surrounding shell of rubber remains intact, whereas the Filastic thread shows a completely unchanged structure. The Filastic threads give a strong impression that an entirely new product is concerned, in which the rubber and cotton are in some way fused together into a homogeneous whole. To these remarks Hauser added that he hoped that he had been able to demonstrate conclusively that the product was new in character, and any imitation could always be detected by microscopic methods.

Definition of Impregnation

These photographs and remarks show clearly that it is now possible to impregnate cotton deeply and in fact completely with latex, the latex penetrating each fiber in such a way that each fibril constituting the individual fibers is covered with rubber and thus is united with the adjacent fibrils.

This is the significance which must be attached to the term *impregnation* in distinction to the term *rubberizing*, whereby the fibers are to a great extent only coated superficially and the fibers thus locked together.

Figure 1

The effect of thorough impregnation with latex is to change the nature of the fibers constituting the threads, whether they are of plant, animal, or mineral origin and whether they are natural or artificial. It makes it possible to produce new types of textiles having unique mechanical and physical properties and at the same time resistant to chemical reagents, molds, etc.

The general name *Filastic* has been given to textiles of this character, the individual types being distinguished by such terms as Filastic cotton, Filastic jute, Filastic wool, Filastic asbestos, Filastic rayon, etc.

Difficulties

The difficulties which have been encountered and which have been overcome arise on the one hand from the nature of textiles and on the other hand from the

nature of latex itself. Thread ordinarily supplied by the cotton manufacturer is twisted tightly, and this hinders impregnation, particularly when the twisting is complicated, as in the case of cord and cabled cord. It has been found that this tight twisting is unnecessary, for the rubber binds the fibers together as well as does twisting. Therefore, slightly twisted yarn has been used for impregnation.

Waxes, gums, and fats which are present in unwashed or unbleached fibers offer resistance to the penetration of latex, and it is necessary to remove them by a suitable boiling or scouring operation. But even with these precautions the problem should not be regarded as solved.

If impregnation by latex is looked upon as a process analogous to dyeing, one might be inclined to believe that it is only a surface effect as opposed to penetration, and that the problem is one of surface tension, which can be solved by the use of wetting agents. Likewise by analogy with methods employed in dyeing, it has been believed that by immersion of a fabric in a latex bath and application of pressure to the surface of the liquid, penetration takes place; in fact, it has been claimed that by increasing the pressure to 100 kg. or more per sq. cm. better results are obtained.

There is no basis for all this, and it is an error to compare a latex bath with a dye bath for the simple reason that the two baths differ in one fundamental respect, *viz.*, the latex bath is coagulable. It is this property of a latex bath which makes the problem of impregnation so difficult, for every factor which promotes coagulation at the point of contact with the fibers acts in opposition to further penetration; a film of rubber is a much greater obstacle than is wax or fat, and it is necessary at any cost to prevent the formation of such films. This is the fundamental principle which has guided us in solving the problem.

The Filastic Process

Since one of the chief causes of the coagulation of latex, at least of Hevea latex, is acidity, it was evident that particular attention would have to be paid to this phenomenon in any investigation of the subject. As is well known, the older ideas of acidity and alkalinity have given way to the more exact concept of a continuous acidity-alkalinity, in which the neutrality point corresponds to pure water. The so-called p_H value is a precise measure of the acidity-alkalinity in terms of the concentration in cation-grams of hydrogen per liter.

In pure water this concentration is 0.0000001, *i. e.*, the p_H value is 7. In a decinormal solution of hydrochloric acid this concentration is 0.1, *i. e.*, the p_H value is 1. In normal sodium hydroxide solution, the concentration is 0.00000000000001, *i. e.*, the p_H value is 14. A p_H value is regarded as acidic when it is below 7, which is the p_H of pure water; as alkaline when it is above 7. Various methods are available for measuring p_H values more or less sensitively.

It has been shown that the p_H value of textile fibers is acidic, *i. e.*, it lies between 3.5 and 4. In this case the p_H value means the p_H value of the moisture in the fibers. It will therefore be readily understood that the greater the penetration of latex into such fibers, the greater its tendency to coagulate. The p_H values of commercial latices are alkaline, the p_H value of diluted Revertex is 11.4. It is possible to change the p_H value of fibers, or that of a latex bath, or both simultaneously. The author has found that when the p_H value of the bath and that of the fibers have the same value or nearly the same value, conditions are most favorable for impregnation. The p_H value can be adjusted either by changing that of the fibers, or by changing that of the impregnating bath, or by changing both at once. With Hevea latex it is easier to operate with an alkaline p_H value, so that here the acidic p_H value of the

fibers should be changed; with Funtumnia latex, which is stable when acidic, adjustment is easy. The p_H value of Hevea latex can be acidic if a stabilizing agent is present.

Attention may be called in passing to the great advantages for certain purposes in the use of Funtumnia latex instead of Hevea latex, and it is unfortunate that it is at the present time impossible to procure enough Funtumnia latex for use in a practical way.

The effect of a substance in adjusting the p_H value is wholly independent of its action as a wetting agent, and it is purely a matter of chance that certain substances are active in both senses, and that there are good wetting agents whose p_H values

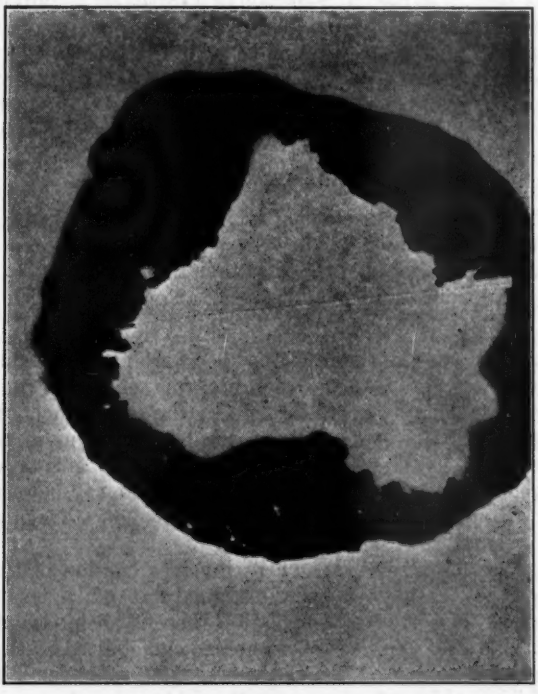

Figure 2

are such that they act in the opposite way to that desired. Among commercial products, Hygrolithe has an acidic p_H value of 5 and Nekal BX, an alkaline p_H value of 8, although their wetting powers are almost the same. On the other hand, Hygrolithe, Sulfo 2D, and Saprotin have the same p_H value of 5, but the wetting power of Hygrolithe is greater than that of Sulfo 2D and that of Saprotin is negligible.

When conditions have been rendered favorable to impregnation, as will be pointed out later, the actual process of impregnation is ready to be carried out. This is favored also by removing in a vacuum the air which is in the textile. Penetration is accelerated by pressure on the surface of the bath. There are, however, other difficulties to be overcome.

In the first place, it must not be forgotten that friction induces coagulation. In virtue of the fundamental principle which has been discussed, friction between the latex and fibers should be kept at a mimimum, and only a moderate pressure should be exerted on the surface of the bath so that the rate of penetration is not too great. It may be mentioned that the use of very high pressures, *e. g.*, of the order of 100 kg. per sq. cm. or even greater, as suggested by certain authors, seems to be impracticable. The use of such pressures increases the rate of penetration and consequently the frictional forces, and can only be unfavorable to good penetration.

There is one factor in particular which is of great importance, *viz.*, the time during which the latex and the textile are in contact with each other, for although a moderate pressure favors the first stage of penetration, the progress of this latter phenomenon is only slow. In the impregnation of a textile by a solution of rubber in a volatile solvent, evaporation of the solvent fixes the rubber on the fibers, whereas with an aqueous dispersion such as latex this is not true; when the textile is withdrawn from the bath, the latex tends to drain off and thus to be removed from the fibers. If it is a question of impregnating spools, which is the method employed for thread or yarn, the lower part of a spool becomes enriched in latex while the upper part becomes impoverished.

A process has been developed for:

1. Prolonging the time of contact of latex and textile, an operation which is indispensable for perfect impregnation
2. Overcoming the tendency of the latex to drain away
3. Fixing the latex on the fibers by means of an operation which may be termed *maturation*.

When this process is used for thread, the spools are placed on spindles on a disc which rotates in a vertical plane. As a result of this rotation of the disc, any latex which tends to drain away is absorbed again by the same spool. By turning the disc in a moist ammoniacal atmosphere, the latex remains in the liquid state for a more or less long period, which is controlled by the degree of humidity in the air and the ammonia content of the latter, both of which can be regulated. Penetration of latex among the fibers proceeds during this first stage of the maturation process.

The second phase of the process, which involves fixation of the latex on the fibers, is based on the fact that between the original state of dispersion of the rubber in the latex and its final state of coagulation there is an intermediate state, the "gel" state. In this gel state the rubber remains immobilized on the fibers, and no longer separates from the latter; yet the impregnated spool can still be unwound, an operation which could not be done were the rubber already coagulated. When the spool is unwound and the thread is passed into a coagulating bath, this so-called rubber gel is converted into a true coagulum, and the contraction which takes place by reduction in diameter of the thread completes the penetration of the rubber among the fibers.

The foregoing discussion has pointed out the difficulties which have been encountered in impregnating textiles with latex, and has also pointed out the way in which these difficulties have been overcome. It is needless to add that the ultimate practical development of these methods has been slow and thorough.

Filastic Threads

Thread treated by the Filastic method differs completely from thread impregnated with solutions. Such threads have a very high rubber content, which at

times is over 50 per cent. This rubber is uniformly distributed from the center to the outside. In contrast to thread impregnated by solutions, which are tacky, even when their rubber content is only 4 per cent, Filastic thread is perfectly dry, and can be woven without difficulty.

Latex rubber, as has been pointed out many times, is so resistant to atmospheric agents that frequently it need not be vulcanized; nevertheless, in some cases Filastic thread should be vulcanized. Accordingly, there is the problem of incorporating vulcanizing agents, including sulfur, accelerators, and activators. It has been found possible to disperse these substances uniformly within the thread structure, not only by using substances which are soluble in water but by using substances in the colloidal state.

Another unusual property of Filastic products should be mentioned. Although latex does not penetrate the textile in its original form, the new type of textile absorbs latex with great facility, and the product can be impregnated a second time in a bath containing substances employed for the purpose of modifying the chemical, physical, or mechanical properties imparted by the first impregnating bath. A very interesting property of Filastic fiber is that when it is inserted within a mass of masticated rubber, it unites with it so that it cannot be separated after the combination has been vulcanized. This gives notably superior fabricated products.

Applications of Filastic Products

The use of Filastic thread makes it possible to manufacture a great number of articles in the rubber industry, and furnishes the textile industry with a new type of fabric. It also introduces the use of rubber to other industries, and thus opens other interesting markets for rubberized products.

Filastic products can be used in the form of single threads, which are impermeable, do not rot, and are resistant to molds. An individual thread of very large size will give a shoe lacing which is tougher than ordinary leather lacing, and since the Filastic thread is so compact, it is unnecessary to provide it with ferrules. Fish nets, tennis nets, etc., manufactured from Filastic thread, are free of any tendency to rot.

When these threads are twisted or braided, cord and rope with no tendency to rot are obtained. They can also be used for braiding electric cables and for braided hose which are resistant to abrasion, oils, and acids. When vulcanized, these braided coverings unite with the adjacent rubber. When used as braid between layers of rubber, Filastic cords improve the quality of hose, and it is impossible to separate the braid from the adjacent rubber.

In the form of web cord they enter into the manufacture of pneumatic tires and thus impart valuable properties to the carcass, such as increased strength and freedom from tendency to rot.

Filastic fabrics resistant to chemical agents are of interest in filtration work. When impregnated a second time, plied together, and vulcanized in a press, they give joints which are resistant to high temperatures and to chemical agents.

By weaving with multiple superposed warps and subsequent vulcanization in a press, it is possible to manufacture soles having resistance to wear 1.6 times as great as the best ordinary soles, and they do not slip as do the latter.

Transmission and conveyor belting can be manufactured in the same way. The adhesion of such belting is almost four times as great as that of ordinary rubber belting, and the resistance to abrasion and to chemical agents is particularly noteworthy.

[Following this contribution is another entitled "Transmission and Conveyor Belting Manufactured from Woven Textiles Impregnated Thoroughly with Latex." In that paper, the same author discusses in detail the manufacture of various types of belting from Filastic textiles with compounded rubber latex, by impregnation of the cotton previous to weaving into fabric, under the conditions already described as essential. Such belting is claimed to wear better, to have higher coefficients of friction, to transmit more power, to absorb less water, to be more flexible and elastic, to stretch less, and to have greater resistance to acids, alkalies, and oils than corresponding belts made with untreated cotton fabric.]

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The Deposition of Rubber on to Textile Fibers

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A review of the literature of the application of rubber to textiles shows a lack of any systematic work on this subject and very little mention of the fundamental problems and principles concerned. Admittedly, a large amount of work has been carried out on wetting agents and allied substances,[1] directed towards obtaining penetration of rubber latex into textile material, and minor investigations have achieved some success in the application of rubber to specific textile materials, *e. g.*, carpets,[2] to achieve specific results. The broad problem, however, remains unattacked. This paper describes the preliminary results obtained from a research designed in some respects to fill this gap.

For reasons which will be apparent from the acknowledgments at the end of this paper, the raw materials of this investigation were rubber latex (natural dispersion) and wool. The use of solid raw rubber and solvent solutions thereof, while not being ruled out, was rejected as being of less interest and value for the purpose of this work; wet processes are in use in the textile industries and are preferable for many reasons to solvent processes. The fact that wool was the particular textile concerned raised several points of some importance in the approach to the problems. In the first place, wool is an expensive raw material compared with cotton, artificial silk, and other fibers. For this reason, it appears undesirable to use it as a filler or reinforcing material for rubber in the same way, for example, as cotton is used to a large extent. If the predominant substance in the product is to be rubber, then there is no advantage in using wool, in preference to cotton or other fibers. Secondly, wool has certain valuable and unique properties, and any application of rubber to wool should therefore be aimed presumably at preserving as much as possible those desirable qualities. On the other side, there is the harshness, tackiness, and drag of a "rubber surface" which the textile man finds very objectionable. If, therefore, a textile rather than a rubber material is to be produced from rubber and wool, then these characteristics of rubber should be avoided at all costs.

On analyzing the objectionable rubbery surface drag, it appeared it was the dried film of rubber latex that was the cause. This led to the idea of avoiding "evaporation" methods entirely. Incidentally, this avoids also, to a large extent, as will be apparent later, the unwettability of textiles (wool in particular) by latex, which presents such a problem. The only alternative to an evaporation process is deposition.

Dyestuffs are applied to textiles from colloidal solution by a deposition process, but, as far as the author is aware, no one has hitherto attempted an analogous process in the case of rubber latex. The problem of depositing rubber on to textile fibers involves ultimately finding some means of giving the two surfaces an affinity, the one for the other.

There are several approaches to this problem, and several factors have to be borne in mind.

The first possibility is impregnation of the fiber with a coagulant for rubber latex. In this case no true deposition occurs, but only coagulation of the rubber around the fibers. Actually, it is possible to achieve something along these lines, but control is difficult and results are unsatisfactory.

The particles of rubber in alkaline latex are normally negatively charged, and will therefore deposit on a positively charged surface. A compound adsorbed by both rubber and textile would provide the necessary affinity and "bond." The so-called "cationic soaps," recently developed on a commercial scale,[3] constitute a material of considerable value.

The ordinary soap substances are compounds consisting of a hydrocarbon chain with hydrophilic head. In water, the positive ion of this substance is the metal, the negative or anion is the long hydrocarbon chain and hydrophilic head. The cationic soaps are the converse of this, the positive ion being the long chain, the negative being a halide, sulfate, or other anionic group. Generally speaking, the hydrophilic group attached to the long chain of carbon atoms is a quaternary ammonium, sulfonium, or phosphonium group; cetylpyridinium bromide and dodecyltrimethylammonium bromide are typical cationic soaps.

These cationic soaps are strongly adsorbed by textile surfaces—particularly by wool—and by reason of the positive charge of the adsorbed, *i. e.*, long-chain, ion give the fiber surface such a charge. On immersing fibers, treated with one of these cationic soaps, in rubber latex consisting of negatively charged particles, deposition of rubber occurs as would be expected. Furthermore, the molecule of soap contains an aliphatic chain which is soluble in the rubber, thus providing a bond between fiber and rubber surface. At the same time, such soaps have to some extent surface-active properties manifested as increasing wettability.

To summarize, therefore, cationic soaps have four properties rendering them excellent material for the problem in hand, *viz.*, a positively charged adsorbable ion, a group adsorbed by textile surfaces, a group soluble in rubber hydrocarbon, and also some wetting properties.

Pursuing the theoretical argument further, there is no reason why the compound should not be applied to the rubber first and the textile afterwards. It has been possible to prepare a latex of which the particles carry an adsorbed layer of cationic soap and which deposits rubber directly on to textile fibers.

The results so far obtained will now be described in detail. The work is classified for convenience into the following parts:

1. The behavior of textile fibers towards cationic soaps, and the deposition of rubber on to fibers so treated
2. The behavior of cationic soaps towards rubber latex
3. The deposition on to textile fibers of rubber latex treated with a cationic soap
4. Alternative methods of causing deposition of rubber on to fibers.

This last section will be published at a later date.

A number of cationic soap compounds have been investigated, as stated, but most of the results reported in this paper have been obtained with a commercially available product, Fixanol, marketed by Imperial Chemical Industries.

I. THE BEHAVIOR OF TEXTILE FIBERS TOWARDS CATIONIC SOAPS AND THE DEPOSITION OF RUBBER ON TO FIBERS SO TREATED

In this part, it is proposed to deal almost exclusively with wool, but justification for the broader title will be found in a concluding section, where data are recorded regarding other fibers, such as jute, flax, cotton, artificial silk, etc.

Adsorption of Cationic Soaps by Wool

When wool fibers are immersed in a solution of a cationic soap in water, the soap is adsorbed by the fibers. The rate of adsorption and quantity adsorbed depend on a number of factors such as p_H, concentration, and temperature of the solution, time of immersion, and previous history of the wool sample.

A number of measurements have been carried out; the determination of the percentage adsorbed, as measured by reduction in concentration of residual liquid, has been made by a method employing rubber latex. This method will be described in Part II.

In the following results, adsorption has been carried out at a constant ratio of weight of wool to volume of solution of 4 grams to 50 cc.

A wool fabric extracted with alcohol and light petroleum was immersed in 0.1-per cent solutions of various p_H values at room temperature for 15 min. The percentages of soap adsorbed by the wool at p_H values of 3.0, 6.0, and 10.0 were, respectively, 0.125, 0.625, and 0.812. Similar results were obtained for a chlorinated wool (chlorine content 1.3 per cent), in top form, immersed in a 1-per cent solution at 45° for 5 hrs; the percentages adsorbed at p_H 3.7, 5.3, and 8.1 were 2.38, 4.25, and 7.70, respectively. The increased adsorption in alkaline solution is very marked—a fact explained by the increased electronegative character of the wool surface in alkaline solution.

An increase of temperature has a large effect; an extracted wool fabric immersed in a 1-per cent solution adsorbed, in 4 hrs., 1 per cent at room temperature and 4.50 per cent at 45°; the corresponding figures for 30 hrs.' immersion were 3.26 and 6.25 per cent.

The rate of adsorption from a 1-per cent solution by an extracted wool fabric at 45° is indicated by the following data: percentages adsorbed in $\frac{1}{2}$, 1, $2\frac{1}{2}$, and 6 hrs. were 1.87, 2.32, 3.63, and 4.38, respectively.

In the course of this work it became apparent that the previous history of the sample under test affected its behavior towards cationic soaps. On investigation, it was found that various treatments, *e. g.*, chlorination, brought about marked changes. Table I gives the results on two samples of wool before and after chlorination.

TABLE I

		Per Cent Adsorption Before	Per Cent Adsorption After
	(*a*) Adsorption in 0.1-Per Cent Solution for 15 Min. at Room Temperature		
p_H	Acid	0.125	0.50
	Approx. neutral	0.625	0.812
	Alkaline	0.812	>1.06
	(*b*) Adsorption in 1.0-Per Cent Solution at 45°		
Time:	$\frac{1}{2}$ hour	1.87	2.32
	1 hour	2.32	3.00

Reference will be made to these data at a later stage when the deposition of rubber is discussed.

Wetting Measurements

Before passing on to a study of treated wool and the deposition of rubber thereon, some results obtained on the wettability of wool will be discussed.

The measurement of wettability[4] is beset with difficulties, and it is not proposed to discuss the subject in detail at this juncture. Numerous methods have been put forward from time to time. There are two simple methods: first, to measure the time it takes for small squares of fabric to sink when placed on the surface of the liquid in question; second, to measure the time taken for a drop of liquid to disperse when applied to a fabric.

Another method consists in totally immersing in the liquid a piece of fabric or hank of yarn, which is attached to what amounts to a hydrometer. When the fabric is wet, the whole system comes to a steady and floating position. Before the solid is wet, more or less air is trapped and buoys the system up. The time-displacement curve is supposed to give a measure of wettability. This method has to commend it the fact that in practice, more often than not, fabric is wetted by total immersion in the liquid.

The measurement of interfacial tension between a solid, existing in such a form as to have a large surface area, and a liquid, by determining the pressure required to force the liquid through the pores of the solid, can also be applied to yarns. A hank of yarn is immersed in the liquid for a given time and then centrifuged. In a constant centrifugal force for a given time the weight of liquid retained by the yarn is a measure of the interfacial tension.

A method has been developed which arose out of a consideration of two of the methods above described, *i. e.*, the sinking time method and the hydrometer method. A $1^1/_4$-in. square of fabric, supported in a light metal clamp, is suspended in a vertical position from one arm of a balance beam and above the solution under investigation. The level of the liquid is raised until its surface just touches the lower edge of the fabric. The deflection of the balance arm is observed at intervals of 15 or 30 seconds, and curves are obtained for a given solution against a given fabric at a given setting of the restoring force of the balance arm. These give an indication of the wettability. The deflection of the balance arm arises from the increase in weight of the fabric as the liquid penetrates it, the penetration of the liquid being due to the rise in the capillary-like spaces of the fabric. For capillary rise to occur, the surface of the fibers must be wetted. Two factors come into play: (*a*) the amount of rise; (*b*) the rate of rise. The former is dependent on pore size and surface tension; the latter, on the wetting power of liquid and wettability of fiber surface, in both of which time of contact plays a major part.

The following is a more detailed analysis of the method. The fabric touches the surface; a small amount of liquid is taken up; this increases the weight of the fabric, which sinks; a further portion of the fabric is then presented to the liquid; a further rise takes place, followed by sinking of the fabric again; the process continues until all the fabric is wet. There is, however, the restoring force of the balance arm and the apparent loss of weight of that portion of the fabric immersed in the solution, against both of which the fabric is weighed. The rate of deflection of the arm, therefore, diminishes, and the deflection reaches a final equilibrium figure. It is concluded that the rate of deflection measures only the rate of rise. If the statement, made above, that "the amount of rise depends on pore size and surface tension, and the rate of rise, on the wetting power of the liquid and the wettability of the fiber surface" is correct, then this method measures predominantly wetting.

Using this instrument, the results shown in Table II have been obtained for a wool fabric before and after chlorination; the effect on the wetting figure of treatment with a cationic soap for varying times is also given.

It is known that chlorination increases the wettability of the wool fibers greatly; the interesting effect, however, illustrated by the above data, is the increase of wet-

tability of unchlorinated wool by a cationic soap, and yet in the case of a chlorinated wool a decrease of wettability is produced. It is apparent that the difference in the rate of adsorption by chlorinated wool recorded above is accompanied by other differences. This alteration of wettability suggests that the orientation of the molecule at the surface is reversed; the aliphatic chain is presumably outermost in the case of chlorinated wool.

TABLE II

Time and Temperature of Immersion in 1-Per Cent Solution of Cationic Soap	Wetting Figure[a]	
	Before Chlorination	After Chlorination
Control—nil	0	18.0
1 hr. at 45°	14.0	2.0
4 hrs. at 45°	20.8	1.0
30 hrs. at 45°	10.4	0.6
4 hrs. at 20°	11.2	2.4
30 hrs. at 20°	14.4	1.2

[a] The wetting figure is the depth to which the pattern sank in 90 seconds into distilled water. A high figure indicates high wettability.

Deposition of Rubber on to Pretreated Wool

On bringing wool treated with a cationic soap in contact with rubber latex, deposition of rubber on to the fibers takes place, as previously stated. A correlation, however, between rubber deposition and adsorption of soap is not found. This can be explained by the fact that it is only the molecules of soap that are on the surface of the fibers that can play a part in rubber deposition. It need hardly be pointed out that the rubber particles are too large to enter the fibers. If the time of immersion has been long, the alkalinity high, or the solution dilute, a greater proportion of the adsorbed cationic soap enters the fiber. Therefore, to procure satisfactory deposition of rubber, it is necessary to employ comparatively concentrated solutions and make the time of immersion short.

It is proposed not to discuss in detail the precise practical details of the application of the cationic soap, but to deal with the deposition of rubber on to fibers which have been pretreated with cationic soap by a method which gives satisfactory results.

The discussion will be confined to a description of the results obtained on the actual deposition process; in the case of fabrics and yarns, details of practical methods of treatment and the properties of the products obtained are deferred to a later publication.

(*a*) *Fabrics.*—In the case of fabrics, the pretreated wool is immersed in the latex for the required time, squeezed, washed in running water under standard conditions, hydro-extracted, and dried. Subsequent determination of the rubber content gives a strict measure of the deposition. The following results explain this point more clearly.

TABLE III

Latex Treatment of Fabric	Rubber Content	
	Untreated Wool	Pretreated Wool
Immersed in 5 per cent latex, squeezed, and dried	3–4 per cent	12 per cent
Immersed in 5 per cent latex, squeezed, washed in water, and dried	0.25 per cent	10 per cent

The resistance to washing immediately after removing from the latex bath is a characteristic of this process and indicates that a true deposition has been brought about.

(*b*) *Yarns.*—In this case, the yarn is handled in hank form either in a manner analogous to that described for fabric or by rotating in a bath until complete exhaustion or nearly complete exhaustion occurs. This latter method is that now used exclusively and, as will be apparent, is particularly advantageous.

As stated previously, chlorination of the wool increases the amount of rubber deposited subsequently. Other means are available, *e. g.*, treatment with hydrogen peroxide or heat-treatment; the normal carbonizing process has also been found to produce the desired effect.

It was at one time suggested that the p_H of the water extract of the wool might give an indication of the deposition likely to occur, but experiments did not bear out this contention; it will be realized that the alkalinity and other ingredients of the latex can be adjusted in accordance with any variation in the original wool, providing that the actual amount of soluble matter is not great.

A number of experiments were carried out on a bulk quantity of suitably pretreated yarn to determine as far as possible the optimum composition of the latex. In these experiments a standard technic was evolved, ensuring reproducibility of mechanical handling of hanks of yarn. Observation was made of the rate and completeness of exhaustion and permanence of deposit, a determination of rubber content being carried out on the dried yarn. The four factors of preliminary wetting out of the yarn, rubber content, alkalinity, and volume of the latex employed have been thoroughly investigated and have been shown to provide means of controlling the rate and completeness of exhaustion.

Examination by Means of Microscope of Sections Cut from Rubber-Treated Yarns.—It is desirable to have some idea of the nature of the deposit of rubber on the fibers. Calculation shows that for fibers of 20 μ diameter and rubber particles of 2 μ diameter, 5 per cent of rubber by weight will cover only 17–20 per cent of the surface of the fibers. The cutting of sections is beset with difficulties, since the majority of the reagents used swell or dissolve the rubber. It has been found possible to prepare sections by using a freezing microtome. These sections show that the rubber is present mostly in the form of patches 2 μ to 4 μ in thickness. Further details of the method and the results obtained will be published at a later date.

Behavior towards Cationic Soaps of Fibers Other than Wool

The adsorption of a cationic soap from a 0.1-per cent solution by various fibers has been determined at three p_H values, the ratio of fibers to solution being kept constant at 4 g. per 50 cc. The fibers in each case except for those of viscose and celanese were extracted with alcohol and light petroleum and thoroughly washed with water and dried before carrying out the test. The data for a sample of wool before and after chlorination are appended for comparison.

TABLE IV

Fiber	Per Cent Adsorbed in 15 Min. at Room Temperature		
	Acid	Approx. Neutral	Alkaline
Cotton	0.75	>1.06	>1.06
Jute	>0.875	>1.06	>1.06
Flax	0.50	0.713	0.725
Kapok	>0.875	...	>1.06
Viscose	0.188	0.50	0.55
Celanese	0.125	0.313	0.55
Wool	0.125	0.625	0.812
Wool (chlorinated)	0.50	0.812	>1.06

These figures indicate clearly that the cationic soap is adsorbed more strongly by some fibers than others, but to some extent by all. Adsorption is strongest in alkaline solution in the case of all fibers.

An experiment was carried out to try and duplicate the results obtained for wool (as recorded above) in the case of a bleached cotton fabric. The following data show the similarity:

TABLE V

Latex Treatment	Per Cent of Rubber on Fabric Untreated	Treated
Padded 5 per cent latex and dried	6.7	9.5
Immersed in 5 per cent latex for 1/2 hour, squeezed, and dried	6.0	14.5
Immersed in 5 per cent latex for 1/2 hour, washed in water, squeezed, and dried	0.3	12.0

Other experiments on jute, artificial silk, flax, and kapok have shown that deposition of rubber occurs under conditions similar to those found for wool.

Discussion

From the foregoing results the following facts are established. Cationic soap compounds are adsorbed by all textile fibers; adsorption is greatest in alkaline solution[5] and at an elevated temperature. In the case of wool, not only do such treatments as chlorination and oxidation by hydrogen peroxide increase the rate of adsorption, but it is apparent that the orientation of the cation is modified. The suggestion is that these treatments render the surface more hydrophilic and thus determine that the soap cation orients itself with the hydrophilic head firmly attached to the fiber surface. The aliphatic chain is, in consequence, outermost.

Turning to the deposition of rubber, it is seen that wool treated with a cationic soap and, therefore, positively charged, attracts the negatively charged particles of rubber in latex, which are discharged. Consequently, a deposit of rubber is formed on the fibers. This deposition is sufficiently definite and irreversible to enable exhaustion of the latex dispersion to take place and, furthermore, the fibers can be rinsed before drying without appreciable loss of rubber.

II. THE BEHAVIOR OF CATIONIC SOAPS TOWARDS LATEX

When a solution of a cationic soap is added to preserved natural or concentrated latex, the phenomena of gelation, flocculation, and coagulation occur, according to the rubber content and other factors.

Gelling

It is not proposed to consider at any length the subject of gelling except to state that the cationic soaps act as gelling agents for rubber latex, and can also be used as delayed-action coagulating and heat-sensitizing agents. For example, the addition of 50 cc. of a 2-per cent solution of a cationic soap to 100 cc. of a 50 per cent latex causes gelation at room temperature; the addition of 25 cc. to the same volume of a 50-per cent latex causes gelation at 70°.

Flocculation

Flocculation takes place if the rubber latex is more dilute. This phenomenon has been the subject of considerable study, and it is proposed to record the results obtained.

The Type and Origin of Latex.—In the first place, the minimum amount of a cationic soap to cause flocculation depends on the type and origin of the latex. A

centrifuged latex requires less to flocculate it than a natural latex, and a dialyzed latex still less—*i. e.*, at the same rubber content. The method of carrying out these determinations is to observe flocculation in a series of test tubes containing the same volume of latex to which has been added an equal volume of solutions of cationic soap of increasing concentration.

The following figures are the number of cc. of 1-per cent solution required to flocculate 5 cc. of various latices at 5-per cent dry rubber content: centrifugally concentrated latex <0.5; ditto (compounded with vulcanizing ingredients) 0.75; natural latex (similarly compounded) 1; a creamed latex (uncompounded) 1.5. These figures clearly illustrate that the presence of non-rubber materials as stabilizers increases the amount of cationic soap required to flocculate the latex.

Rubber Content.—The minimum amount of cationic soap required increases with the rubber content of the latex. A centrifugally concentrated latex compounded with vulcanizing ingredients has a flocculation value (*i. e.*, cc. of 1-per cent solution to flocculate 5 cc. of latex) of 0.75 at 5 per cent, 0.875 at 7.5 per cent, 1 at 10 per cent, and 1.5 at 15-per cent dry rubber content.

Alkalinity and p_H.—One of the interesting points regarding flocculation of latex by cationic soaps is that the p_H is not a determining factor. Complete flocculation has been produced at all p_H values between 3 and 11. The percentage of soap required, however, does vary with the p_H.

The following experiment was carried out. A quantity of a centrifugally concentrated latex was diluted to a dry rubber content of 10 per cent with the addition of sufficient anionic soap stabilizer to enable it to be acidified without coagulation. Portions of this 10 per cent latex were diluted with 2 per cent acetic acid and half-normal ammonia solution, respectively, to a dry rubber content of 5 per cent. The acid latex required 1.75 cc. and the alkaline latex, 8 cc. of 0.1 per cent cationic soap to flocculate 5 cc.

Stabilizers and Thickeners.—As would be imagined, the presence of stabilizing agents and such like in the latex has a retarding effect on the phenomenon and more of the reagent is required. This has already been shown to be the case for latices of various origins. For example, a flocculation value of 1 cc. is increased, by the addition of 4 per cent (by weight on the rubber in the latex) of a sulfonated higher alcohol soap, to 2.25, by the addition of 8 per cent to 3, and by the addition of 10 per cent to a figure greater than 4.

The Type of Cationic Soap Employed.—In all the above data, as stated, the soap employed has been a commercial product composed principally of cetylpyridinium bromide. Some determinations have been made of the floculation values of several compounds in 1-per cent solution in water against a latex of standard alkalinity and dry rubber content of 5 per cent, with the following results: cetylpyridinium bromide (pure) 0.5; cetyltrimethylammonium bromide 0.5; cetyldimethylsulfonium methyl sulfate 0.5; dodecyldimethylammonium methyl sulfate 0.5; phenylbenzyldimethylammonium chloride >5. In the case of dicetyldimethylammonium bromide coagulum was produced at 0.25 cc. but no clear serum until 1 or 1.5 cc. and then the aggregation was coagulation, and not flocculation.

There are several points of interest in these results. In the first place, the dicetyl compound produces coagulation rather than flocculation, which suggests that the two aliphatic chains are linking the particles together. Secondly, the compound without a long chain has no flocculating action. Finally, all the compounds of similar molecular configuration have approximately the same flocculating power, the anion being without influence.

A Method for the Determination of the Concentration of a Cationic Soap in a Solution

In the course of the above experiments it was observed that the concentration of cationic soap required to cause flocculation of a given latex was critical. This fact suggested a method for determining, with a fair degree of accuracy and rapidity, the percentage concentration of an unknown solution, knowing, of course, the nature of the compound in such solution. This method has proved useful in obtaining the data required for adsorption of the soap by fibers as recorded in Part I of this paper.

The method is extremely flexible, since concentration, volume, and if necessary, p_H can be adjusted to give the required sensitivity and accuracy. A range of test tubes is prepared from known and unknown solutions and comparison of rate of separation or opacity of serum enables a value to be obtained rapidly. Correction may be necessary for any change in the flocculating power brought about by the water-soluble substances associated with the fibers.

The Production of a Moldable Flocculated Paste

Just as by means of the well-known flocculating agents a moldable paste is obtained from latex, so cationic soaps can be used for this purpose. The pastes so produced are particularly stable, and retain their crumbiness at quite low water contents. A satisfactory paste can be prepared by the addition of 40 parts (by volume) of a 0.4-per cent solution of cationic soap to 10 parts of a 50 per cent latex, the mixing being carried out at 80–90°, with constant stirring. The flocculated paste is separated from the water by a simple filtration process to a water content of 30–50 per cent.

The Addition of Excess of a Cationic Soap to Rubber Latex

If a quantity of a cationic soap in excess of that required to cause flocculation is added to rubber latex, it has been observed that a stable latex is obtained. This latex is best prepared by addition of the raw latex to a solution of the soap rather than *vice versa*.

A study has been made of the minimum quantity of soap required for the production of this latex and several facts have been established.

As in the case of flocculation, so in the case of the production of this stable latex, p_H is of no consequence. Stable latices, containing excess of cationic soap, with only a slight tendency to cream, can be obtained in either alkaline or acid media. The presence of ingredients of a stabilizing character in the original latex renders the production of the latex difficult; more of the reagent is required. Purification of the latex by dialysis[6] or centrifuging reduces considerably this amount. As a general rule, however, no difficulty is experienced in the case of raw latex. When an endeavor is made to carry out experiments on vulcanized or vulcanizable latices, the problem is more complex, and it appears essential to employ a purified material.

A number of samples of latex have been examined and the minimum weight of cationic soap required to produce 100 cc. of stable latex of 5-per cent dry rubber content has been determined, with the following results: dialyzed natural latex 0.30 g.; centrifuged natural latex 0.35 g.; heat-concentrated natural latex >1.00 g.; creamed natural latex >0.80 g.; dialyzed vulcanized latex 0.70 g.; ditto, further dialyzed 0.50 g.; single centrifuged vulcanized latex 0.75 g.; ditto, dialyzed 0.475 g.; triple centrifuged vulcanized latex 0.275 g. The effect of purification is clearly indicated.

The minimum amounts of three cationic soap compounds required to stabilize a given latex indicate that, in this respect, as well as in flocculation power, they behave quantitatively in a similar manner. Thus, 0.25 g. is required of either cetylpyridinium bromide or cetyltrimethylammonium bromide, and 0.30 g. of cetyldimethylsulfonium methyl sulfate.

Cataphoresis Experiments.—In order to determine how the stable latex produced by addition of excess of cationic soap differed from a normal latex, it appeared desirable to carry out some measurements of cataphoresis migration on latices of the two types to determine at least the sign of the charge carried by the rubber particle. No great accuracy was aimed at in these determinations. The apparatus used consisted of the usual U-tube, inverted to take account of the fact that rubber is lighter than water. Approximately 100 volts d. c. were applied across two platinum electrodes. The intermicellar liquid was prepared for each latex to have approximately the same alkalinity and conductivity.

Two series of three latices were examined. The first consisted of a centrifugally concentrated latex stabilized with Igepon T. This was diluted with appropriate solutions to give 5-per cent latices of p_H values approximately 3, 8, and 10.5. In all three cases the particles migrated to the anode, *i. e.*, the charge is negative. The second consisted of the same latex stabilized with a cationic soap and brought to the same three p_H values as for the first series. In all these three cases the particles proved to be positively charged. It is thus evident that excess of cationic soap has reversed the charge of the latex particles.

Note on the Stability of This Latex of Reversed Charge.—No systematic tests have been carried out on the properties of the positively charged latex, except to study deposition of rubber from it on to fibers. This work is described in the next section of this paper. There are several facts, however, which are known, and could have been forecast on theoretical grounds. The latex of reversed charge is flocculated by all the usual stabilizers (soaps, and so forth) for latex. In fact, in an analogous manner to the determination of the concentrations of cationic soap solutions by the use of natural latex, the concentration of ordinary soaps and stabilizers can be determined by the use of latex of reversed charge.

The Preparation of Positively Charged Dispersions of Other Substances

The replacement of ordinary (anionic) soaps and stabilizers by a cationic soap in the dispersion of solids and liquids in water enables a suspension of positively charged particles to be equally readily obtained. Such materials as paraffin wax, carbon black, pigments, sulfur, as well as resins and Neoprene latex, can be dispersed in this manner, for use as such, or for addition to rubber latex of reversed charge.

Discussion

The so-called charge carried by the particle of dispersed solid in aqueous medium is determined in the last resort by the character of the surface of that particle. That surface may consist of ions arising from the substance of the particle, or of adsorbed ions of a substance present in the aqueous solution. The stability of the particle depends on the charge, and the sign of the charge depends on the ion attached to or adsorbed by the particle. In certain circumstances the sign of the charge will depend on the p_H.

In natural rubber latex, the rubber particles carry an adsorbed layer of protein substance, which in alkaline solution, gives them a negative charge. Since the

protein is the responsible substance, coagulation takes place at the isoelectric point of the protein. It is possible to acidify latex to give a stable dispersion, the particles of which, according to the literature, are positively charged.[7] This correlates with the well-known behavior of protein as a colloidal electrolyte. The reversal of charge is not so easily demonstrated with ammonia-preserved latex.

The addition of an anionic soap compound to latex stabilizes the particles against coagulation by acids and, as has been shown, renders the negative charge permanent and unaffected, in sign, by p_H. The assumption is that the surface layer surrounding the particles has become composed of soap ions, consisting of an aliphatic chain and hydrophilic head. In the same way, excess of a cationic soap gives the particles a permanent positive charge. The explanation is the same except that the adsorbed soap ions are now cations.

The facts recorded above give a clear picture of the mechanism of flocculation and stabilization of latex by cationic soap compounds. The only point open to question is whether or not the adsorbed protein layer is displaced by the soap.

The obvious lines of development are experiments on the addition of the cationic soap to fresh latex and the effects of centrifuging, dialysis, the new cataphoresis method,[8] and similar processes on such latex. These experiments are, of course, best carried out on the plantations, and would be directed to the production of concentrates, consisting of particles of reversed charge and stabilized with cationic soaps.

III. THE DEPOSITION ON TO TEXTILE FIBERS OF RUBBER LATEX TREATED WITH A CATIONIC SOAP

In Section II of this paper was described the production of a stable latex of reversed charge, stabilization being effected by a cationic soap.

With the knowledge that negatively charged latex deposits on to fibers treated with a cationic soap, it was suggested that, theoretically, if a latex could be produced, of which the particles carried a coating of cationic soap, deposition of rubber would occur from it direct on to untreated fibers. With such a latex available, the preliminary experiment was one to correspond with that carried out in the case of pretreated wool (described above). Pieces of wool fabric, before and after chlorination, were immersed in latices of 5-per cent dry rubber content for 30 min., removed, and washed, squeezed, hydro-extracted, and dried, according to standard procedure. Table VI gives the results obtained.

TABLE VI

Rubber Latex (5-Per Cent D. R. C.)			Per Cent Rubber on Fabric	
Stabilizer	Particle Charge	p_H	Unchlorinated	Chlorinated
Nil	Neg.	Alkaline	0	0
Cationic soap	Pos.	Alkaline	6.0	11.5
Cationic soap	Pos.	Acid	Trace	1.9

The above table indicates the superiority of a chlorinated fabric and the necessity for an alkaline latex for deposition to take place—facts which accord satisfactorily with previous experiments and theoretical speculations. Thus it is established that a latex of reversed charge deposits rubber directly on to fibers.

The next step was to carry out experiments to ascertain whether deposition could be made to take place to complete exhaustion of the bath in the case of yarns. In other words, it was desired to show parallel phenomena in the two processes. It is obvious that a modification of the latex is preferable to a pretreatment of the wool, provided that the rubberizing can be carried out at any stage in the course of manu-

facture by this one-bath process. Attention has thus been directed to a theoretical study both of the preparation of the stable latex, described above, and of the conditions for direct deposition on to wool in various states. It has been found possible to evolve an exhaustion process analogous to that described for pretreated wool. In addition to the factors previously examined in the latter process, other questions have been considered. For example, it may be required to treat wool after a scouring process with or without drying, after a milling process, or after an acid dyeing process. In other words, wool containing acids, alkali, or soap may be involved.

The latex of reversed charge is stable towards acids, as previously stated, but deposition is retarded, in which case a correspondingly more alkaline latex must be used or a more alkaline preliminary wetting-out. In the case of there being residual soap present in wool from the scour, this will find its way into the latex bath and cause flocculation with reduction in the efficiency of the exhaustion. Experiments have shown that this flocculation can be reduced, if not eliminated, by employing a latex containing more cationic soap.

An alkaline wool will cause exhaustion to take place normally, but, due to the swelling of the fibers, the deposit tends to be not permanent; this effect has been referred to previously. It can be overcome by previous washing of the yarn, reduction of alkalinity of latex, or by the use of formalin, which reduces fiber swelling.

As regards such factors as rubber content and volume of latex bath, similar remarks apply as in the case of the rubberizing of wool pretreated with cationic soap.

Furthermore, experiments have shown that deposition of rubber occurs directly on to fibers other than wool, *e. g.*, cotton, jute, artificial silk, and so forth.

It is possible to pursue the theoretical argument further and consider the converse of the process just described. This means the employment of a latex stabilized with anionic soap, *i. e.*, negatively charged in acid solution, using the fact that surfaces generally have a slight electropositive character in acid solution.

Preliminary experiments have been carried out and confirm the correctness of this argument, but deposition, so far, has not been found to be more than 50–60 per cent. Further work is in progress, and it is hoped to report this and other results in Part IV of this paper to be published at a later date. Suffice it to say that the degree of adsorption of the stabilizing anionic soap by the fiber surface as well as p_H and fiber pretreatment are determining factors.

SUMMARY

(*a*) The preliminary results obtained in an investigation of the deposition of rubber from latex on to textile fibers are recorded. Methods of deposition have been considered in order to avoid the rubbery handle associated with evaporated films of latex.

(*b*) The cationic soap compounds recently produced commercially enable satisfactory deposition to be brought about.

(*c*) Data are given of the adsorption by textile fibers of these compounds.

(*d*) The effect of cationic soap compounds on rubber latex and the production of a latex of reversed charge are described.

(*e*) The two alternative processes for deposition of rubber are discussed: the first employs natural latex in conjunction with textile fibers pretreated with cationic soap; the second employs latex treated with cationic soap in conjunction with untreated fibers.

(*f*) A short discussion of the theoretical basis for the results is given.

Thanks are due to the Councils of the Wool Industries Research Association and

Rubber Growers' Association for permission to publish this paper. The interest and assistance of the Director and staff of the former association have been much appreciated. Acknowledgment is also due to Imperial Chemical Industries, Ltd., for the supply of the cationic soap compounds referred to.

Patent protection for processes described in this paper has been applied for.

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Estimation of the Stability of Rubber Solutions

Manfred Rachner

ERFURT

Various types of rubber products, such as seamless goods and rubberized fabrics, are prepared from rubber solutions and are vulcanized either by the hot or cold process. "Cold vulcanization" is effected either by sulfur chloride vapor or by very dilute solutions of sulfur chloride in solvents such as carbon disulfide, carbon tetrachloride, or benzine. "Hot vulcanization" is carried out by heating with sulfur, organic accelerators, and inorganic substances such as colloidal zinc oxide, to "activate" the accelerators.

To safeguard against any unforeseen difficulties, it is necessary not only to ascertain how much tendency mixtures containing powerful accelerators have to vulcanize, but above all to determine for how long a time a solution remains stable, *i. e.*, does not commence to vulcanize during ordinary use.

To obtain an insight into the practical utility of a mixture, it is in general necessary merely to heat the mixture at 110° C. in a press. A mixture can be regarded without hesitation as satisfactory for practical use if it shows no indication of vulcanization after one hour at this temperature. On the other hand, products prepared from such a solution should as a rule vulcanize fully in 30 min. at 125° C. or perhaps in 40–50 min. at 110° C. In view of this, the practical utility of a mixture is judged by the tendency for incipient vulcanization to take place when the mixture is heated at 70° C. in a press. In the case of solutions of rubber mixtures which contain all ingredients milled into the rubber before the solution is prepared, incipient vulcanization is evident by gelation of the solution, *i. e.*, a change from sol to gel. With mixtures of this kind, incipient vulcanization at 70° C. in a press may be accepted as a reasonable criterion, but in no case should it be regarded as a trustworthy indication of the stability of a solution up to the point of gelation, for the rate of vulcanization of the solution to the point of gel formation, and during gel formation itself, is influenced considerably by the constitution and the concentration of the solvent. The concentration of the solution and the degree of plasticity of the rubber mixture likewise influence gel formation. A test of the dry mixture at 70° C. in a press for incipient vulcanization does not take account of these factors.

The testing method described below gives a far more reliable indication of the probable tendency of a solution to vulcanize, and makes it possible to estimate in advance, at least in an approximate way, the beginning of gel formation when the solution is stored at room temperature or is used in a practical way. The test requires only a few cubic centimeters of solution and is simple to carry out. The procedure involves heating several cubic centimeters of solution on a water bath at 70° C. until the solution gelatinizes. To this end about 1.5 cc. of solution is pipetted into a small bottle with bakelite screw-cap (also provided with a cork 6 × 6.5 mm.). If the same experiment is repeated ten days later, it will be found that in most cases considerably less time is required for a gel to form. Fairly accurate conclusions can be drawn as to the ultimate stability of the solution from the mag-

nitude of this decrease in the time required for a gel to form. For example, if a fresh solution gelatinizes in ten hours, and then after ten days' storage gelatinizes in eight hours, the loss of stability is 20 per cent, so that the solution will remain stable for about 35 or 40 days longer.

Unfortunately, numerous experiments have shown that this fairly uniform progress of vulcanization to the point of actual gelation is not in every case a linear function of the time. Three anomalies in this simple straight line relation have been found.

1. A delay in the onset of vulcanization. When solutions were stored at room or working temperatures, no differences were in general found between the times required for the fresh solutions to gelatinize at 70° C. and the times required for the same solutions to gelatinize under the same conditions after standing for ten days. Accordingly the first ten to fourteen days of standing should be disregarded, and the two experiments should be repeated at the correspondingly later period. Only from these new results is one justified in drawing conclusions as to the general stability of a solution.
2. Rather large deviations from the simple straight-line proportionality are frequently encountered in about the last third of the period during which a solution is still apparently stable. Vulcanization progresses considerably faster than during the first two-thirds of the period of storage.
3. With most rubber mixtures, gelation appears practically spontaneously and without any previous indication by an increase in viscosity. On the contrary, in some cases the solutions become considerably thicker, and especially when mild vulcanization accelerators are present, considerable increases in viscosity of the solutions are evident before the appearance of actual gelation. To a certain extent these increases can be adjusted by subsequent dilution, but it has been found that in general a solution of relatively high concentration gelatinizes sooner than the same solution when more dilute.

Aside from the possibility of being able to foresee the progress of vulcanization of a rubber solution to the point where it gelatinizes, the first test, *i. e.*, with fresh solutions, makes it possible to draw certain important conclusions.

As is known, benzene is still frequently used as solvent, in spite of its poisonous nature, for so-called "self-vulcanizing solutions." It has been found that with many rubber mixtures, benzene solutions of these mixtures gelatinize far sooner than do benzine solutions of the same mixtures. Chloroform solutions gelatinize still sooner. In carbon tetrachloride vulcanization is slower.

These observations are surprisingly similar to experiments described by LeBlanc and Kröger (cf. *Kolloid-Z.*, **33**, 168 (1923)). These investigators studied chiefly vulcanization by sulfur chloride, and found that vulcanization with this reagent in benzene solution took place in approximately one-half the length of time required for vulcanization of the corresponding mixtures in benzine (heptane) solution. Likewise in benzene, vulcanization of a mixture containing sulfur and an accelerator took place in about one-half the length of time required in benzine. No change in this ratio of one to two was observed for a series of mixtures of various compositions. This of course applies only to the general stability of solutions at room and working temperatures. When the solutions are first warmed to 70° C., gelation of a given mixture dissolved in benzene takes place only 30–40 per cent sooner than in benzine. After these solutions have stood for ten days, however, the time required for the benzene solution to gelatinize at 70° becomes so much shorter than that for the fresh benzene solution to gelatinize at the same tempera-

ture that the relative rates of vulcanization of the benzene and benzine solutions at room temperature become as great as one to two.

The observation of chemists of the I. G. Farbenindustrie A.-G. that small proportions of alcohol accelerate the gelation of solutions containing the accelerator Vulkacit P extra N have been in general confirmed. Acetone has a still more pronounced effect in this respect.

The progress of vulcanization was found to be extraordinarily slow when highly purified trichloroethylene was used as solvent. With technically pure trichloroethylene on the contrary, gelation took place far sooner. Nevertheless, the results of hot vulcanization using trichloroethylene are not in accord with the results of vulcanization by sulfur chloride described by LeBlanc and Kröger. But when chloroform was used as solvent the results conformed to one another. Here both cold vulcanization, in accordance with LeBlanc and Kröger, and also hot vulcanization progressed very rapidly. Likewise in carbon tetrachloride the results of hot and cold vulcanization were similar, although in this case more time was required for gelation. As a matter of fact, however, with chloroform and with carbon tetrachloride, no such simple numerical ratio as that between benzene and benzine for both sulfur chloride and sulfur vulcanization was observed.

This influence of the constitution and concentration of the solvent on vulcanization must therefore be taken into account also when the particular rubber mixture concerned contains sulfur, accelerator, and other ingredients necessary for vulcanization.

The method of heating a solution until gelation takes place makes it possible in this way to judge directly the stability of a solution, and thereby to decide upon the suitability of the recipe for technical use.

These tests for incipient vulcanization are recommended not only as aids in judging the behavior of a particular recipe, but also for use as a regular control method, since with more careful control it will frequently be found possible to employ successfully far more active mixtures. It is also possible, among other things, to determine in the production of seamless rubber goods the effect of replenishing with fresh solution the solution used from a given supply. If for example, $^2/_3$ volume of a solution several days old, which at the time gelatinizes in 8 hours at 70° C., is mixed with $^1/_3$ volume of fresh solution, which gelatinizes in 12 hours at 70° C., it will be found that the thoroughly blended mixture will, as calculated, actually begin to gelatinize in about nine hours at 70° C.

The value of a recipe for practical use can be judged by two factors: (1) the rate of vulcanization at 110° C. or at 125° C. of the article prepared by the dipping process, and (2) the stability of the solution at 70° C. to the point of gelation. By repeating the test for incipient vulcanization after ten days as a basis of comparison and then after 20 days, a sufficiently accurate criterion will be had.

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Compression Tests of Vulcanized Rubber

R. Ariano

1. OBJECT OF THE INVESTIGATION

Compression tests[1] are used to a small extent in ordinary control testing of rubber mixtures prepared in the laboratory, but it is not possible with such tests to decide from an examination of various finished products which of the products will give satisfactory service under compression.[2]

Results obtained by this test have been in many cases contradictory, and it is safe to say that their conversion into analytical expressions has led to as many conclusions as there are authors who have worked on the subject.[3] It appears then that the number of variables involved in a compression test is so great, and at the same time these variables are so little understood, that the test is meaningless at present. Naturally then one is induced to study the subject in detail, with the hope of being able to decide on the ultimate possibilities of the test and on the most favorable conditions under which it will give clearly defined results.

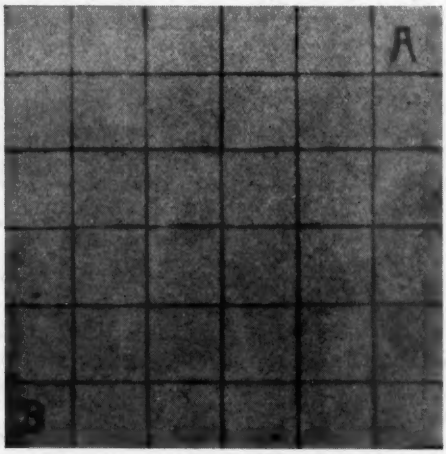


Figure 1—Lattice on the Face of a Cube before Being Deformed

With this in mind, it seemed opportune to determine the distribution of the deformations which take place in cubical test-specimens when their surfaces are lubricated and when they are not, and when the specimens are solid and when they contain holes in various locations.

The standard cube was kept the same in all cases to minimize the possibilities of variations from this point of view. The cubes were prepared from a mixture of slab rubber 100, sulfur 8 (by weight), vulcanized in a press for 30 min. at 100° C., 30 min. at 1 atmosphere steam pressure, 30 min. at 2 atmospheres' steam pressure,

and 25 min. at 3 atmospheres' steam pressure. It was considered unnecessary to repeat the series of tests with other mixtures, since there did not seem to be any good reason why the composition should influence in any essential way the qualitative nature of the phenomena studied.

2. TECHNIC OF TESTING

The cubical test-specimens had sides of 60 cm. After having compressed a cube a photograph was taken of one of its faces, on which had previously been drawn a lattice of numerous squares with sides of about 1 centimeter, parallel to and perpendicular to the direction of compression. The marked faces were also photographed before compression (see Fig. 1). All photographs were taken with a magnification of about 5-fold, so that the distances to be measured were relatively large, and consequently the percentage errors in the measurements were relatively small.

As is known, the end faces of a cube of rubber under compression are curved as a result of friction between the compressing platens (in the present work these were

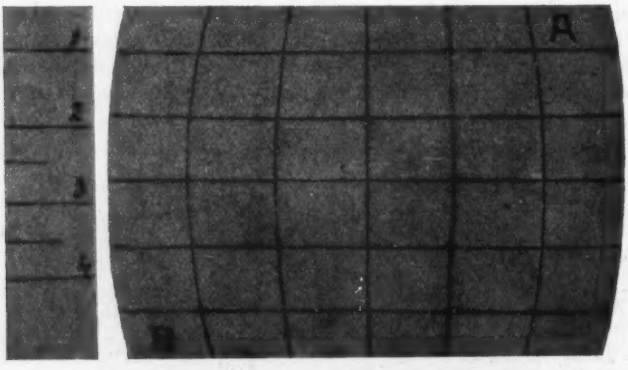


Figure 2—Lattice on the Face of a Cube Deformed by Compressing 18 Per Cent. The Contact Surfaces Were Dry

of iron) and the faces of the cube in contact with them. Accordingly, the photographs are projections of the deformed lattices on a plane parallel to that of the lattice itself before deformation. Reliefs made in this way do not therefore tell much regarding the deformation of the end faces, but it may be assumed that the deformations of the middle plane of the cube parallel to these same surfaces are deducible from the deformation of the end faces.

To find the changes in length which actually occur on the end faces, measurements of the elongation of the sides of the deformed lattice squares were made by placing on these squares transparent paper, and marking progressively, by means of a fine-pointed needle, the positions of the corners of the lattice. In making these measurements, care was taken, by means of gages, to control the initial deformation and prevent the platens from becoming any closer than they were during the first minute of application of the load.

3. EXPERIMENTAL RESULTS

1. Measurements of the Photographs

A. Solid cubes. Compressing surfaces not lubricated. In Fig. 2 is shown a photograph of a cube compressed 18 per cent. It is evident that here the straight

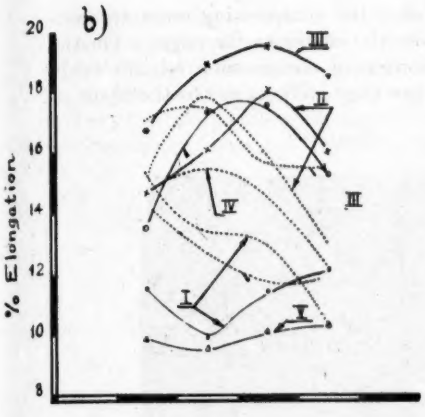
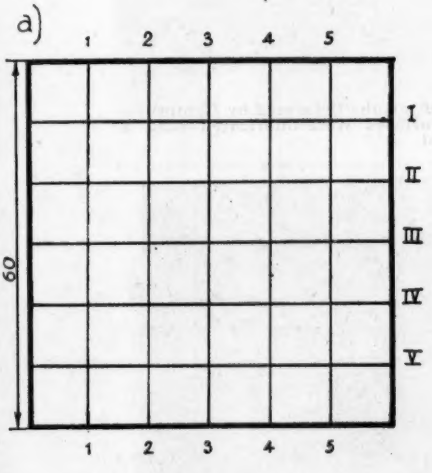
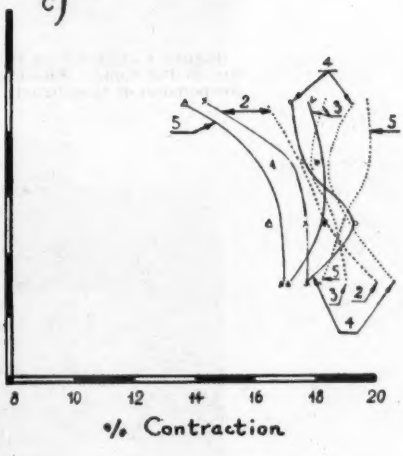
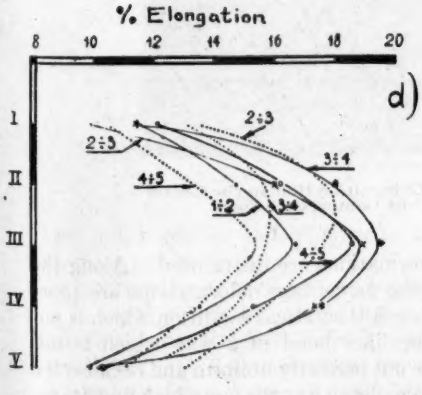


Figure 3—Solid Cube Compressed 18 Per Cent
(a) face of cube with lattice
(b) elongations on the horizontals marked on (a)
(c) local contractions on the verticals marked on (a)
(d) elongations of the vertical bands marked on (a)

——————— dry surfaces
- - - - - - - - contact surfaces lubricated with graphite-glycerol







lines (except the middle line) in the direction of the compressing force are considerably bowed, the curvature increasing from the center to the edges. On the contrary, the lines perpendicular to the direction of compression remain fairly straight, except towards their extremities, where they are concave to the plane of compression.

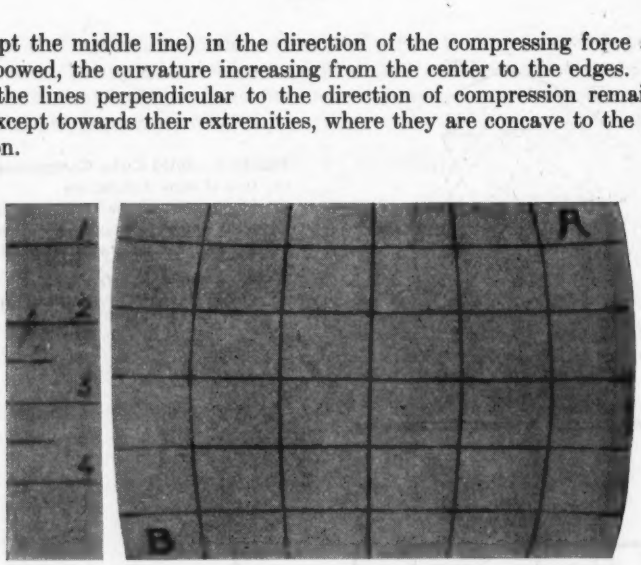


Figure 4—Lattice on the Face of a Cube Deformed by Compressing 18 Per Cent. The Contact Surfaces Were Lubricated with a Suspension of Graphite in Glycerol

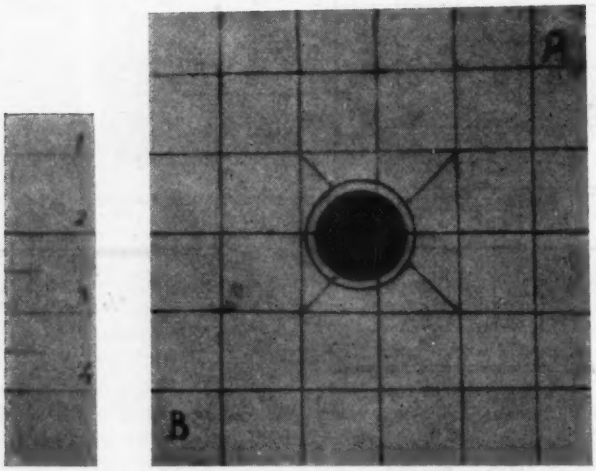


Figure 5—Lattice on the Face of a Cube with a Hole in the Center Normal to the Direction of the Compressive Force

Figure 3 shows the way in which the deformations are distributed. Along the perpendicular line 3, *i. e.*, the middle line, the percentage deformations are practically the same at the various points. This is a theoretical condition which is not actually attained. The other perpendicular lines bend in a way which is not strictly symmetrical because the platens were not perfectly uniform and because the lower platen was fixed while the upper movable platen was the one which first trans-

mitted the load. Naturally this bending results in an increase in the distance, *i. e.*, in less contraction, between the observed points.

Likewise the deformations along the horizontal lines do not show any uniformity, *i. e.*, in the elongation. The two lines next to the platen surfaces are the least deformed; the middle line is deformed the most. This is a logical consequence of the form assumed by the cube. Moreover in the case of the first two lines, deformation

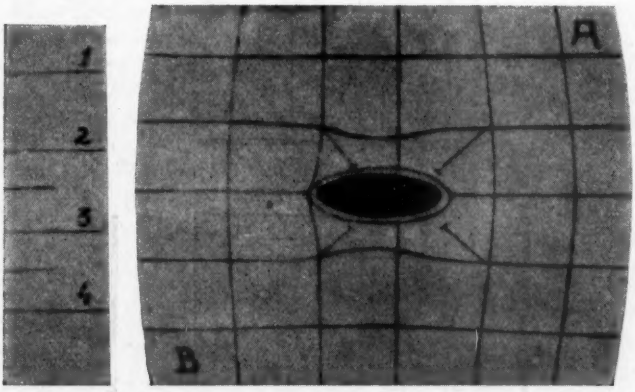


Figure 6—The Cube Shown in Figure 5 When Compressed 18 Per Cent between Platens Not Lubricated

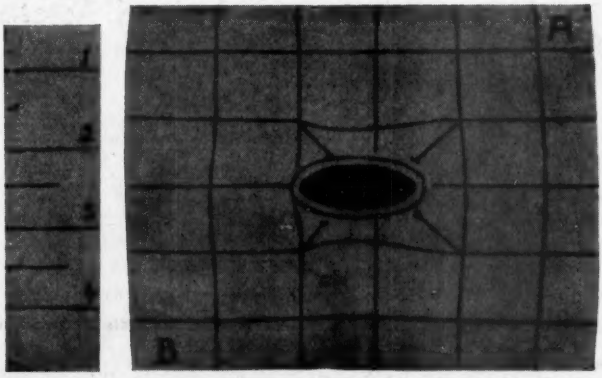


Figure 7—The Cube Shown in Figure 5 When Compressed 18 Per Cent between Lubricated Platens

is least in the middle; in fact, these lines curve at their extremities, with maximum curvatures at their centers.

An examination of variations in breadth of the vertical sections between lines 1, 2, 3, 4, and 5 shows that all these areas have maximum widths corresponding to the middle horizontal line. These maxima correspond to an elongation between 16 and 20 per cent, *i. e.*, of the same order as the maximum contraction.

B. Solid cubes. Faces lubricated with a very fluid film of glycerol containing

graphite in suspension. This lubrication reduced considerably the curvature of the vertical lines, as is evident by comparing the photographs shown in Figs. 2 and 4.

The curves in Fig. 3 show an approach to uniformity in the local deformations along each perpendicular (it is assumed that differences of 1–2 per cent which occur

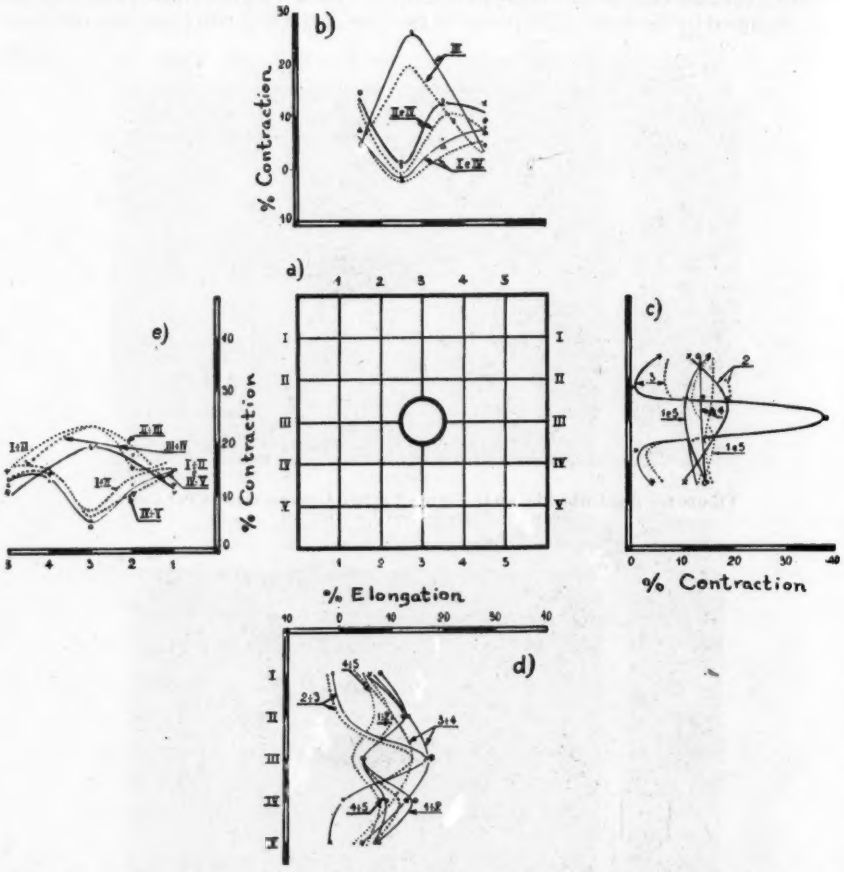


Figure 8—Cube with Hole (10 Mm. Diameter) Having Its Axis Perpendicular to the Direction of the Compressive Force

(a) face of cube with lattice
(b) elongations on the horizontals marked on (a)
(c) local contractions on the verticals marked on (a)
(d) elongations of the vertical bands marked on (a)
(e) contractions of the horizontal bands marked on (a)

———— dry contact surfaces
– – – – – – – – contact surfaces lubricated with graphite-glycerol.

may be errors in the measurements). On the contrary, variations in breadth of the vertical areas retain their central maxima; these maxima are merely slightly less pronounced and the curves are in general a little flattened.

The elongations along the horizontals remain irregular; among other things there is dissymmetry along the test-specimen (shown in Fig. 4), which may be attributable

to the fact that uniformity of the coefficient of friction at all points of contact of rubber and metal is not attained.

C. Cube with hole in center (prepared by burning through the rubber with a red-hot iron disc) of approximately 10-mm. diameter, perpendicular to the compressing force.

Figures 5, 6, and 7 are reproductions of photographs of the face on which the lattice was drawn, both before and after deformation, with the contact surfaces lubricated and not lubricated.

It is evident at once from these photographs that the hole has brought about a disturbance in the deformation, *viz.*, a drawing together of the horizontal lines and a spreading of the vertical ones.

Figure 8 shows that the hole localizes the vertical deformation on the middle line (3). Likewise, as far as the horizontal lines are concerned, the elongation is concentrated on the middle line, *i. e.*, the axis of the hole. Correspondingly the other straight lines show almost no elongation.

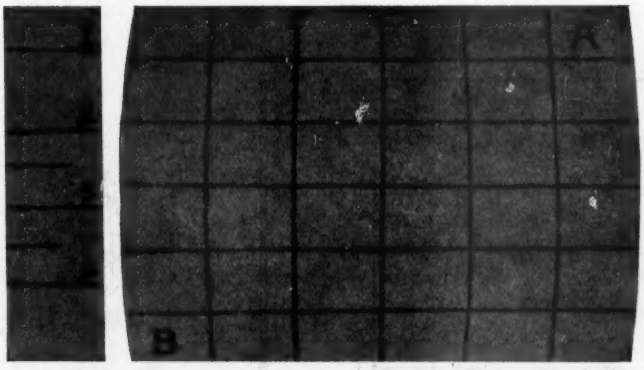


Figure 9—Lattice on the Face of Cube with a Hole in the Center in the Direction of the Compressive Force. Compression 18 Per Cent

The vertical and the horizontal areas show maximum variations in breadth corresponding to the hole when adjacent to the latter and minimum variations when not near the hole. However, the maxima are not any greater than those occurring in the case of samples without a hole.

Here, too, the lubricant tends to make the deformations more uniform, without, however, making them actually constant, as would be expected from a theoretical point of view.

D. Cube with hole (10-mm. diameter) located in the center, with its axis parallel to the direction of the compressive force. No lubrication of the contact faces.

Figures 9 and 10 show that the distribution of the deformations is similar to that in the case of a solid cube compressed likewise on non-lubricated contact faces. It should merely be noted that the deformations of the vertical lines are more nearly alike, and that all show a distinct minimum deformation in the center.

2. Measurement of the Actual Deformations (Measured with the Paper Method Indicated)

Figure 11 gives the results of tests of a cube with a hole having its axis perpendicular to the direction of the compressive force. In this case the deformations of the

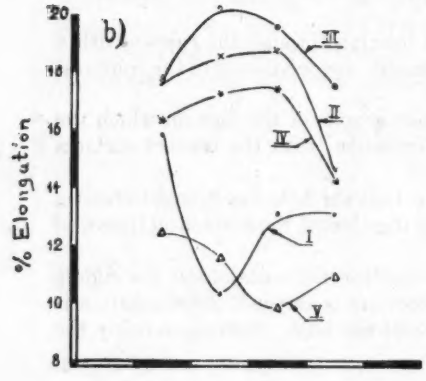
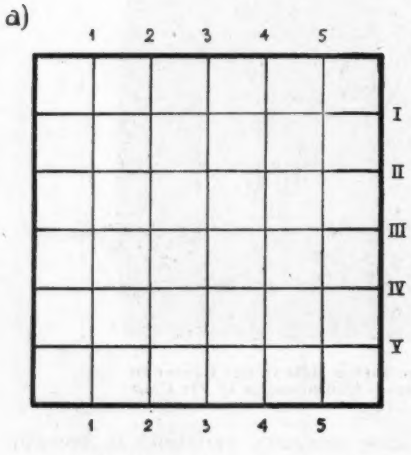
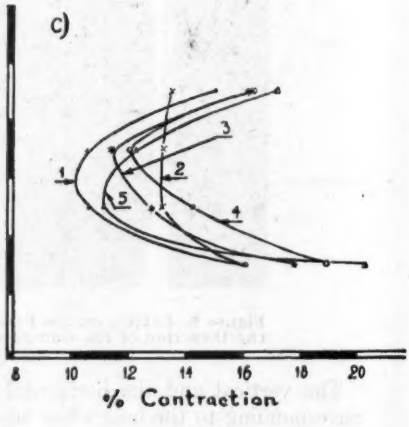


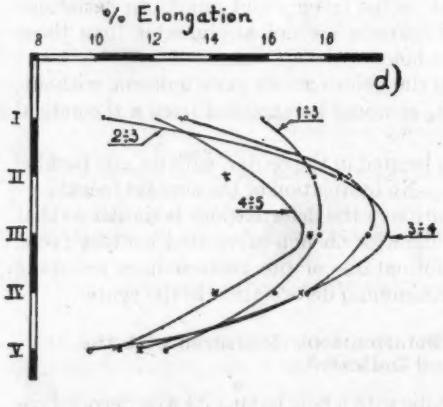
Figure 10—Cube with Hole (10 Mm. Diameter) Having Its Axis Parallel to the Direction of the Compressive Force

(a) face of cube with lattice
(b) local elongations on the horizontals marked on (a)
(c) local contractions on the verticals marked on (a)
(d) elongations of the vertical bands on (a)

All tests were with dry contact surfaces







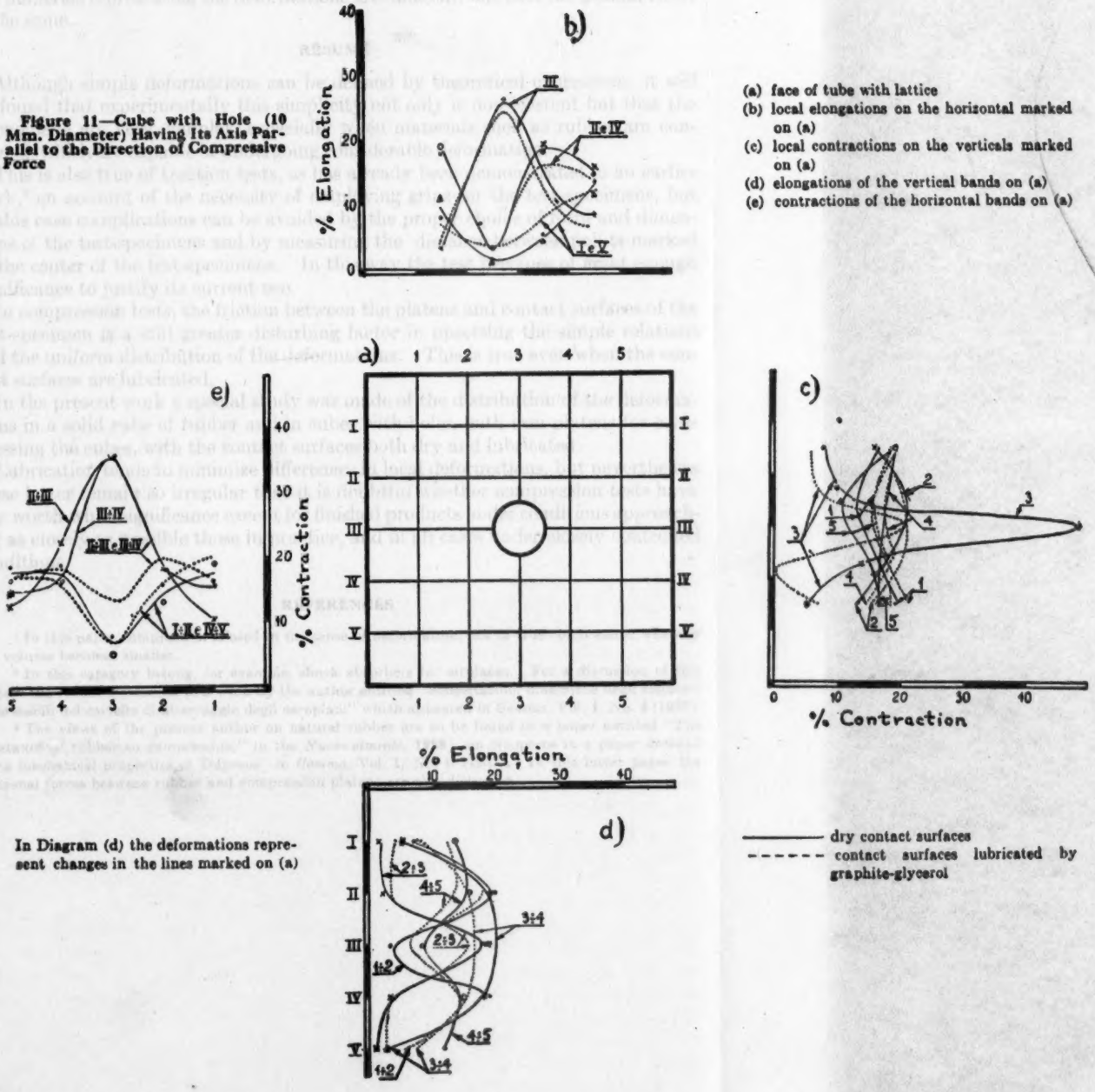


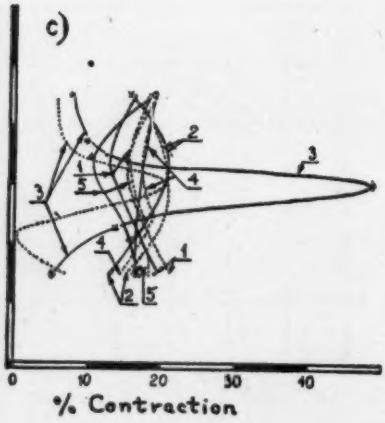
Figure 11—Cube with Hole (10 Mm. Diameter) Having Its Axis Parallel to the Direction of Compressive Force

(a) face of tube with lattice
(b) local elongations on the horizontal marked on (a)
(c) local contractions on the verticals marked on (a)
(d) elongations of the vertical bands on (a)
(e) contractions of the horizontal bands on (a)

In Diagram (d) the deformations represent changes in the lines marked on (a)

——— dry contact surfaces
- - - - - - contact surfaces lubricated by graphite-glycerol

(a) face of tube with lattice
(b) local elongations on the horizontal marked on (a)
(c) local contractions on the verticals marked on (a)
(d) elongations of the vertical bands on (a)
(e) contractions of the horizontal bands on (a)



——— dry contact surfaces
- - - - - - contact surfaces lubricated by graphite-glycerol

face are greatest of all. A comparison with the results shown in Fig. 8 shows that the numerals representing the deformations are different, but that the general effect is the same.

RÉSUMÉ

Although simple deformations can be defined by theoretical expressions, it will be found that experimentally this simplicity not only is non-existent but that the phenomena are very complex, especially when materials such as rubber are concerned, which are capable of undergoing considerable deformation.

This is also true of traction tests, as has already been demonstrated in an earlier work,[3] on account of the necessity of employing grips for the test-specimens, but in this case complications can be avoided by the proper choice of form and dimensions of the test-specimens and by measuring the distance between points marked in the center of the test-specimens. In this way the test becomes of great enough significance to justify its current use.

In compression tests, the friction between the platens and contact surfaces of the test-specimen is a still greater disturbing factor in upsetting the simple relations and the uniform distribution of the deformations. This is true even when the contact surfaces are lubricated.

In the present work a special study was made of the distribution of the deformations in a solid cube of rubber and in cubes with holes, with iron platens for compressing the cubes, with the contact surfaces both dry and lubricated.

Lubrication tends to minimize differences in local deformations, but nevertheless these latter remain so irregular that it is doubtful whether compression tests have any worth-while significance except for finished products under conditions approaching as closely as possible those in practice, and in all cases under closely controlled conditions.

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[1] In this paper compression is used in the sense of deformation, not of true compression whereby the volume becomes smaller.

[2] In this category belong, for example, shock absorbers for airplanes. For a discussion of this subject the reader is referred to a work by the author entitled "Sollecitazioni dinamiche negli elementi deformabili del carrello di atterraggio degli aeroplani" which appeared in *Gomma*, Vol. **1**, No. 4 (1937)

[3] The views of the present author on natural rubber are to be found in a paper entitled "The resistance of rubber to compression," in the *Nuovo cimento*, **1926**; on Neoprene in a paper entitled "The mechanical properties of Duprene" in *Gomma*, Vol. **1**, No. 6 (1937). In this latter paper the frictional forces between rubber and compression platens are also discussed.

[Translated for Rubber Chemistry and Technology from Recherches et Inventions, Vol. 18, No. 275, pages 78–81, April, 1938.]

Some Applications of High-Frequency Electric Currents to the Latex Industry

Henri Leduc

The "radiocoagulation" of latex has been developed in the laboratories of L'Office National des Recherches et Inventions by Dufour and Leduc, who conceived the idea of applying the effect of electric fields of high frequency to rubber latex.

When latex is exposed to the action of an electric field of high frequency, the entire body of liquid is heated uniformly, provided that the electric field itself is uniform. The causes of this heating effect are difficult to ascertain because various phenomena are involved simultaneously, *e. g.*, a dielectric loss in the rubber and a loss by the Joule effect in the serum.

Each of these effects is, according to conditions, the predominant one, *e. g.*, by increasing the conductivity of the serum, electrolytes such as sodium sulfate or ammonium sulfate increase the Joule loss, U^2/R, whereas an increase in the concentration of latex tends to increase the dielectric loss. Finally, since rubber particles are not electrically neutral, they are subject to alternating forces of the electric field, which is a specific effect of the high frequency, and these forces impart to the rubber particles movements throughout the liquid. Now latex can be rendered sensitive to mechanical forces, *i. e.*, some mixtures can be coagulated by slight agitation. Accordingly it is conceivable that a high-frequency electric field, by setting the rubber particles in motion throughout the emulsion, is capable of coagulating a mass of latex exposed to the field.

Latex mixtures can also be made sensitive to heat, *i. e.*, whereas a mixture may be stable at room temperature, it may coagulate rapidly when raised to a certain temperature. This phenomena is a result of chemical action, but as a process of coagulation it is suitable only for the production of thin articles, for unless the mass to be coagulated is thin, considerable time is required for coagulation because of the difficulty in the heat penetrating to the center of the mass to be coagulated. If on the contrary, the mass is exposed to the action of an electric field, it heats immediately throughout, and the chemical coagulating effect due to the heat adds itself to the mechanical coagulating effect due to the movements of the particles brought about by the electric field.

Finally, another advantage of radiocoagulation should be pointed out. If two vessels, A and B, are filled with the same latex mixture, and the mixture in A is coagulated by heating, *e. g.*, by immersion of A in a hot water bath, while the mixture in B is coagulated by a high-frequency electric field, it will be found that the center of coagulum A always tends to be hollow because of a more compact deposit of rubber near the surface of the container, which becomes heated before the internal region does. On the other hand, coagulum B is perfectly homogeneous as a result of uniform coagulation throughout the liquid.

From a practical point of view, radiocoagulation consists therefore of placing in an alternating electric field of high frequency (10,000,000 to 20,000,000 cycles per second, for example) a latex mixture, which may or may not contain the necessary

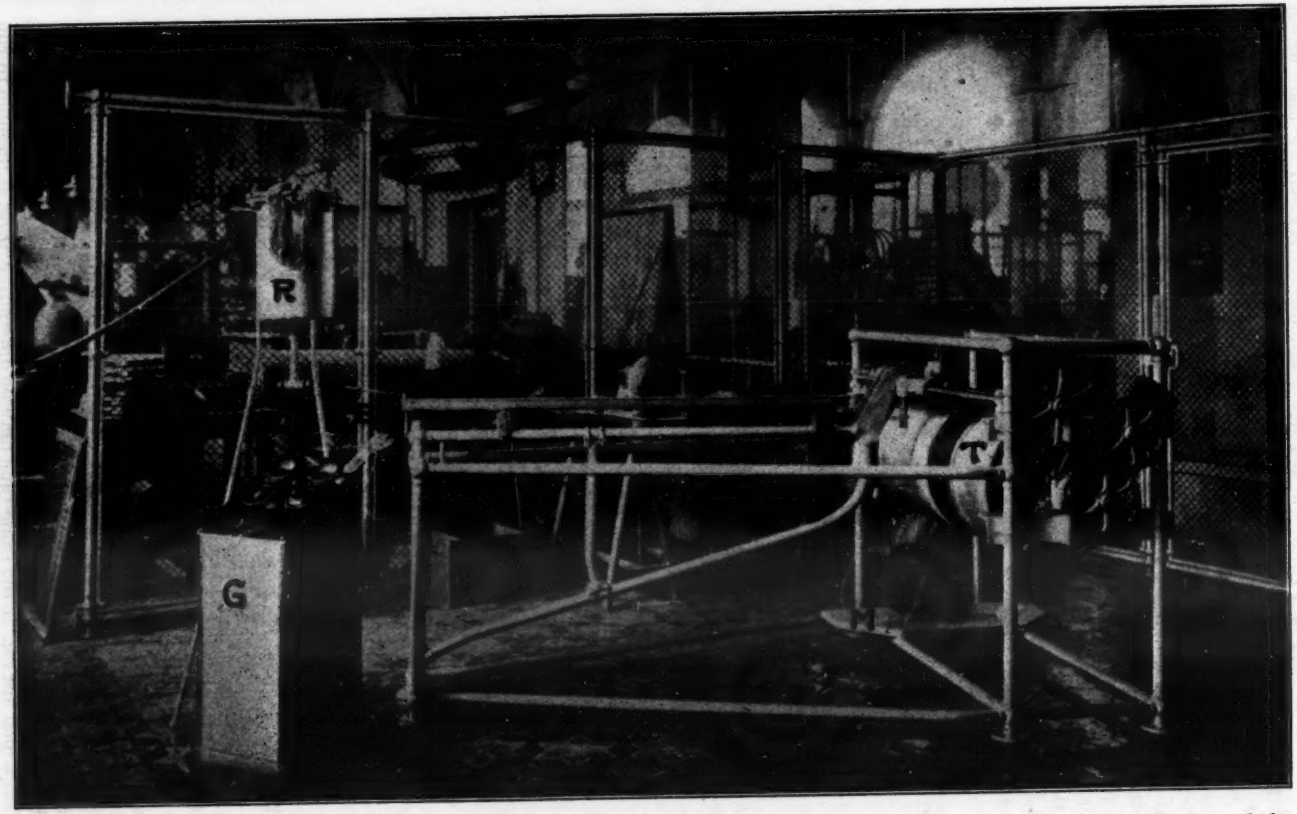

Figure 1—Apparatus for Making Thread from Latex. The Photograph Shows the Latex Reservoir, the Oscillator, the Nozzle, and the "Winding-Off" Drum

vulcanizing agents; as a result the mixture coagulates throughout the mass which is exposed to the electric field, of which the coagulum is in a way the material result. The extensive applications of such a process may be easily imagined.

Manufacture of Latex Thread

If latex flows through a glass tube against which are fixed two electrodes connected with a high-frequency current, the latex coagulates, and the coagulum takes the form of the tube, with a slight contraction corresponding to the exudation of water, which facilitates movement of the coagulated thread through the tube. As the thread issues from the tube, it is necessary only to collect it, dry it, and vulcanize it. These last operations can be made continuous if desirable.

Figure 1a—Detail from Figure 1

The thread which issues from the tube is remarkably firm and compact, but it is still plastic, and it can be changed in cross section and thus striated or otherwise designed, *e. g.*, by passing it between two suitably designed wheels. It is thus possible to form directly the widest variety of cross sections, such as circular, square, flat, etc., and all sizes from the largest to the smallest, whereas by the older processes only round cross sections and of a diameter not exceeding one millimeter can be formed.

The consumption of energy is very small, and an oscillator of 100 watts is sufficient to coagulate fourteen parallel threads (see Fig. 2).

The adaptability of the process is evident from the fact that the diameters of the threads which are run at the same time may be different, *e. g.*, it is possible to run simultaneously threads of 15/10 and 10/10 sizes.

Figure 1 represents a complete equipment for running thread. Latex in reservoir, R, is forced under pressure into the tube, F, along which are fixed electrodes, E, connected with the high frequency generator, G. The thread passes without friction into a trough full of water and thence to the drying drum, T, on which it is wound. This drum is rotated by a motor, M, which operates a mercury contact and thus guarantees constant tension on the threads.

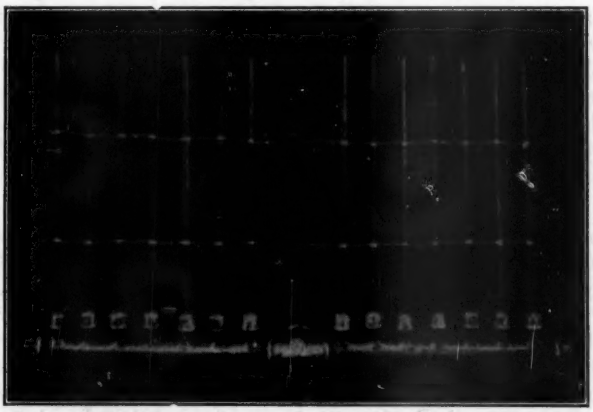

Figure 2—Battery of Tubes for the Manufacture of Latex Thread

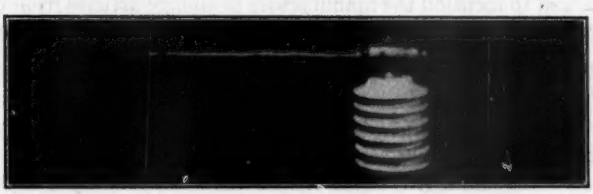

Figure 3—Apparatus for the Manufacture of Latex-Rubber Insulated Wire

Figure 4

Latex Tubing

In this case, the tube is composed of two concentric glass tubes, having between them an annular space through which the latex flows. The electrodes arranged along the system are connected with a high-frequency generator, whereby coagulation is brought about.

Latex Sheets

If the tube through which the coagulum issues is flat, sheets are obtained having dimensions corresponding to those of the opening. By this method, thin products such as rubber films, hospital sheeting, and thicker sheets of various kinds, such as floor-coverings, can be produced.

Rubber-Covered Articles

It is evident that if cotton or silk thread or a wire conductor is run through the tube along with latex, it will be coated with latex, the adhesion of the coating depending on the nature of the thread or wire and the composition of the latex.

The applications of such products are numerous; *e. g.*, cotton threads can be coated with latex to make belts, and wire can be coated with latex for electric lighting cord. In this latter case, the tube is constructed as shown in Fig. 3.

Cellular Articles

If latex contains air bubbles, these are trapped in the coagulum, and it is possible in this way to make sponge articles with open or closed cells, and cellular tubing of the character of bamboo, with cavities containing air or other gas at any desired pressure.

To this end, the conducting tube should be so constructed that a gas can be introduced intermittently into the middle of the latex, *e. g.*, by means of a suitably arranged central nozzle (see Fig. 4). In this way it is possible, by multiplying the number of cores or spindles in an extruding tube, to obtain blocks, sheets, or multitubular cylindrical articles, constituting joints of remarkable flexibility. At this point it is well to mention the manufacture of sponge articles from latex. The processes employed up to the present time are all based on the following principle:

1. Frothing of the latex
2. Coagulation of this froth.

To this end, either a coagulant with delayed action is added to the frothed latex, so that its effect is evident only after a definite time, *e. g.*, 20 min., or else a so-called "dormant" coagulant, the effect of which is manifest only at a certain temperature, is added.

Besides serious inconveniences, these processes are slow, so that the molds are not used economically. Here too, a high-frequency field is of advantage, *i. e.*, if frothed latex of either type is placed in a suitable field, coagulation takes place within a period of time which never exceeds two or three minutes. The solidity of the coagulum and the uniformity of the pores are increased. The output obtained from the molds is also considerably greater, and the operations are quicker and more reliable.

Other Applications

A high-frequency field not only offers a method for coagulating latex when applied to a suitably stabilized product, but by the aid of such a field it is possible to heat quickly and uniformly a large volume of either immobile or agitated latex. Proper equipment can be readily devised for such special applications as the vulcanization of latex in the emulsified state and concentration of the product by bubbling air into a uniformly heated mass of latex.

The foregoing discussion, which is necessarily limited, gives an idea of the resources placed at the disposal of the rubber industry by this new technical process, which has been promptly adopted by the industry.

[Reprinted from Industrial and Engineering Chemistry, Vol. 30, No. 6, pages 704–708, June, 1938.]

Flocculation of Pigment in Carbon Black–Rubber Mixtures

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The Firestone Tire & Rubber Company, Akron, Ohio

NUMEROUS references occur in the literature as to the cause of so-called scorching or burning in rubber-pigment mixes containing no vulcanizing agent. It was suggested (*6*) that this stiffening effect may be caused by flocculation of the pigment particles. Green (*8*) demonstrated a relation between the stiffness and flocculating tendency of pigments in paint mixtures, and Depew and Ruby (*4*) and Green (*7*) suggested that the phenomenon of flocculation may have some relation to the properties of cured rubber mixes which contain pigments, especially carbon black pigments. Grenquist (*9*) reported that carbon black exists in a more or less flocculated condition in vulcanized rubber, and some evidence was presented by Park and Morris (*11*) that mill-scorched batches which exhibit abnormal stiffness possess a structure which suggests that the black has been flocculated.

The increase in stiffness of unvulcanized rubber–carbon black mixes upon standing for periods of several days was mentioned by Stamberger (*13*). Busse and Davies (*2*) presented data showing the effect of heat upon the stiffness of such mixes and mentioned the possible relation between flocculation and increase in stiffness.

In order to throw more light upon the behavior of carbon black in the stiffening of rubber, a series of experiments was planned following the general methods of Busse and Davies, which include heating the sample for various periods of time and attempting to follow the changes in gross physical properties and in the minute structure of the mix.

Stiffening Effect of Heat on Master Batches

To determine quantitatively the effect of heat on the plasticity of master batches, a number of batches containing varying concentrations of rubber channel black were made up and heated in nitrogen for 8 hours at 132° C. The plasticities of these stocks were then determined on the extrusion plastometer (*5*).

Table I shows, in agreement with the results of Busse and

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Davies that, with the exception of pure gum rubber, all of the samples were markedly stiffened by heating.

Such stiffening action of heat on master batches is not confined to channel black batches but may also be obtained on master batches of much coarser black. An example is the ac-

TABLE I. AVERAGE EFFLUX RATE

Carbon Black per 100 Vol. Rubber	At 3260 Lb./Sq. In. (230 Kg./Sq. Cm.) Pressure		Carbon Black per 100 Vol. Rubber	At 8120 Lb./Sq. In. (570 Kg./Sq. Cm.) Pressure	
	Before heating	After heating[a]		Before heating	After heating[a]
Volumes	*Cc./min.*	*Cc./min.*	*Volumes*	*Cc./min.*	*Cc./min.*
0	242	268	30	7.6	0.4
2	169	110	40	1.0	0.007
4	134	60.5			
8	103	12.3			
12	63.5	5.0			
16	28	2.8			
20	8.4	0.4			
25	2.3	0.1			

[a] In nitrogen 8 hours at 132° C.

tion of heat on a Gastex master batch. When a master batch containing 67 parts of Gastex (the product of a free flame process) per 100 parts of rubber was heated under the same conditions as were used for channel black, the stiffening was much less but quite definite as measured on the extrusion plastometer. This effect is indicated in Table II where a 40 per cent Gastex master batch heated for 8 hours is compared with a 40 per cent channel black batch heated for 4 hours.

TABLE II. EFFECT OF HEAT ON MASTER BATCHES

Stock[a]	Treatment	Time	Mass	Efflux Rate
		Sec.	*Grams*	*Cc./min.*
40 % channel black	Unheated	59.7	9.07	7.8
	Heated 4 hr. at 270° C.	105.9	9.56	4.7
40% Gastex	Unheated	4.6	9.91	133
	Heated 8 hr. at 270° C.	3.4	8.78	112

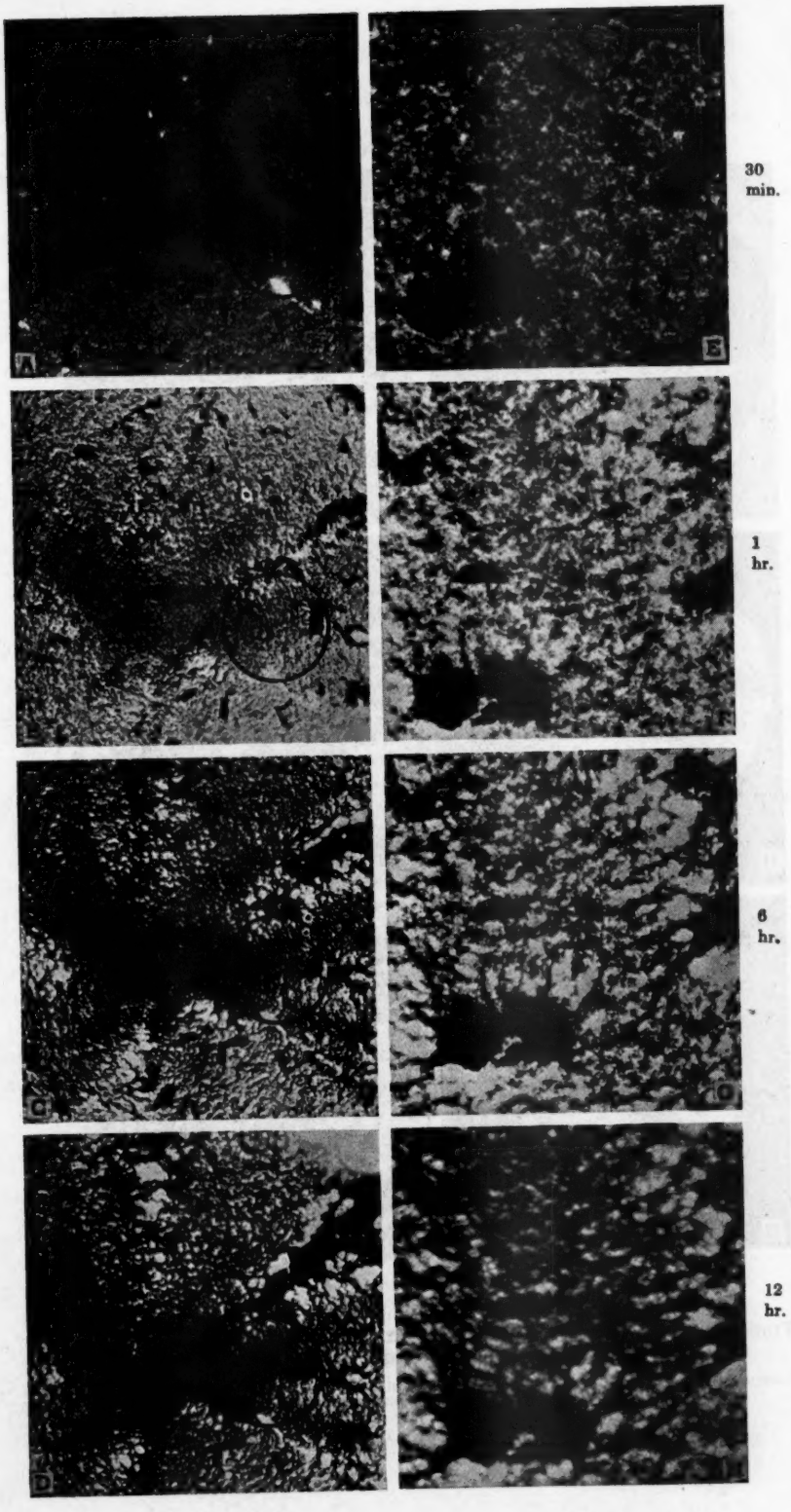
[a] Temperature, 100° C.; pressure, 6050 pounds per square inch (425 kg. per sq. cm.); gravity of stock, 1.16.

It was found impossible to show microscopically any change in structure in these heated master batches, either by the polishing method of Roninger (*12*) or by the squeeze-out method of Allen (*1*). In the first case the method is designed to show only gross discontinuities in

CAPTION FOR FIGURE 1 (See opposite page)

FIGURE 1. SUCCESSIVE STAGES OF FLOCCULATION OF A SAMPLE OF CHANNEL BLACK-RUBBER MIXTURE DURING HEATING AT 135° C.

Composition: rubber, 100; channel carbon black, 8 parts by volume. The areas marked by circles (in *A* to *D*) are shown at higher magnification in *E* to *H*.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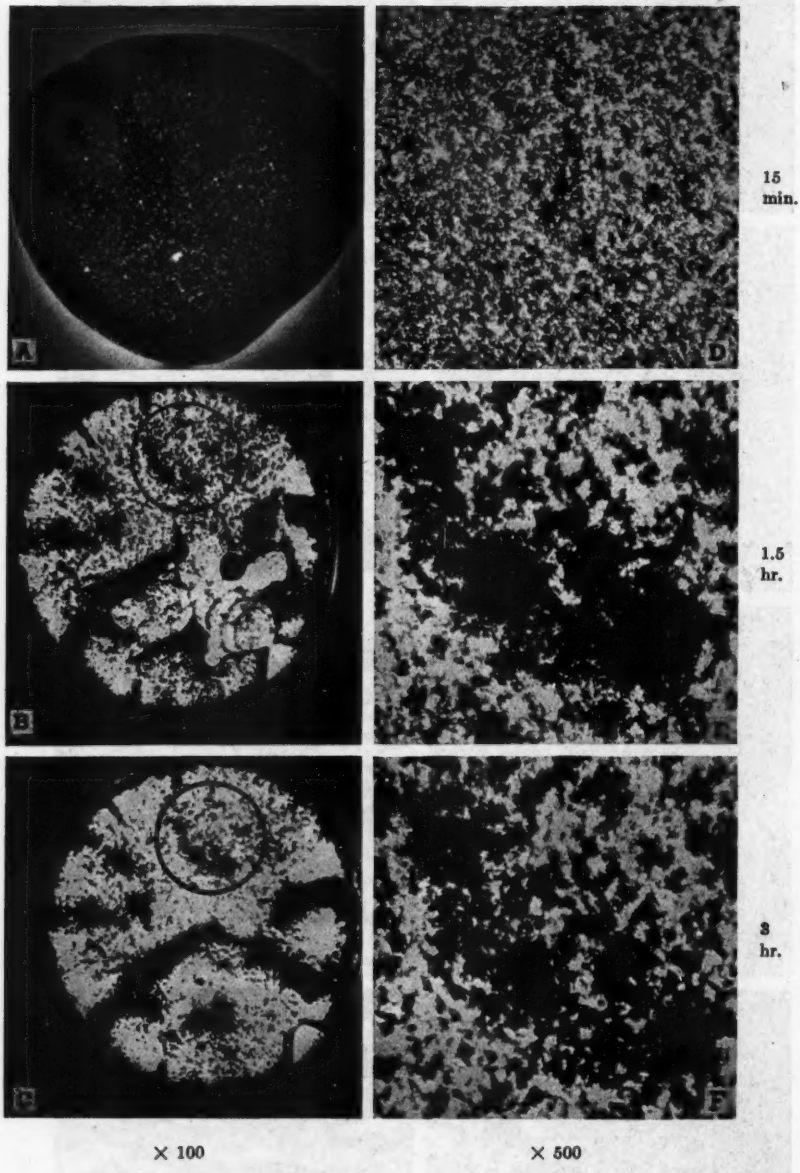


FIGURE 2. SUCCESSIVE STAGES OF FLOCCULATION OF A MIXTURE OF GASTEX CARBON BLACK AND RUBBER DURING HEATING AT 135° C.

Composition: rubber, 100; Gastex, 8 parts by volume. The areas marked by the circles (in *A* to *C*) are shown at higher magnification in *D* to *F*.

a master batch; in the latter, the shearing force on the sample at the high temperature necessary to squeeze the pellet into a transparent sheet probably obliterates any fine structure that is present.

By squeezing out an unheated sample in the *Quetschkammer* or squeezing chamber of Dannenberg (*3*) and then heating it in an oven, it was found possible to follow the progress of flocculation under the microscope.

Figure 1*A* shows a master batch squeezed out in a chamber and heated for 30 minutes to cause it to flow out and become translucent. Figure 1*B* represents the same sample after being heated at 135° C. in an oven for 1 hour; *C* and *D* show the same sample heated for 6 and 12 hours, respectively. The increasing flocculation is evident in these photo-

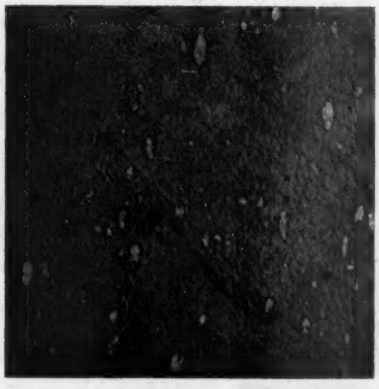


FIGURE 3. POLISHED SECTION OF NORMALLY MIXED MASTER BATCH CONTAINING 40 PER CENT CARBON BLACK BY WEIGHT

graphs at 100 diameters, but a magnification of 500 shows the details much more clearly. Figure 1*E* shows the sample after the preliminary heating, and *F*, *G*, and *H* represent the progress of flocculation at periods of 1, 6, and 12 hours, respectively.

Flocculation may be followed similarly in a Gastex master batch. Figure 2*A* shows at 100 magnifications an 8-volume stock after being heated for 15 minutes in the squeezing chamber; *B* and *C* represent the same sample after being heated 1.5 and 3 hours, respectively. Figures 2*D*, *E*, and *F* show this same sample at 500 magnifications. Here also the formation of floccules is plainly evident.

As has been mentioned, this change in structure brought about by the heat treatment is accompanied by an increase in stiffness of the material, making it difficult or, in some cases, impossible to obtain a smooth homogeneous mixture

upon further mastication of the batch. Since these carbon black master batches are usually processed in the factory by mixing further with rubber to form a so-called final batch, the increased and variable stiffness caused by overheating of the master batch during milling or piling of the stock in a hot condition may constitute a difficulty for the plant operator.

An examination of the condition of such final batches has been made to determine in what state these stiffened master batches exist in the final stock.

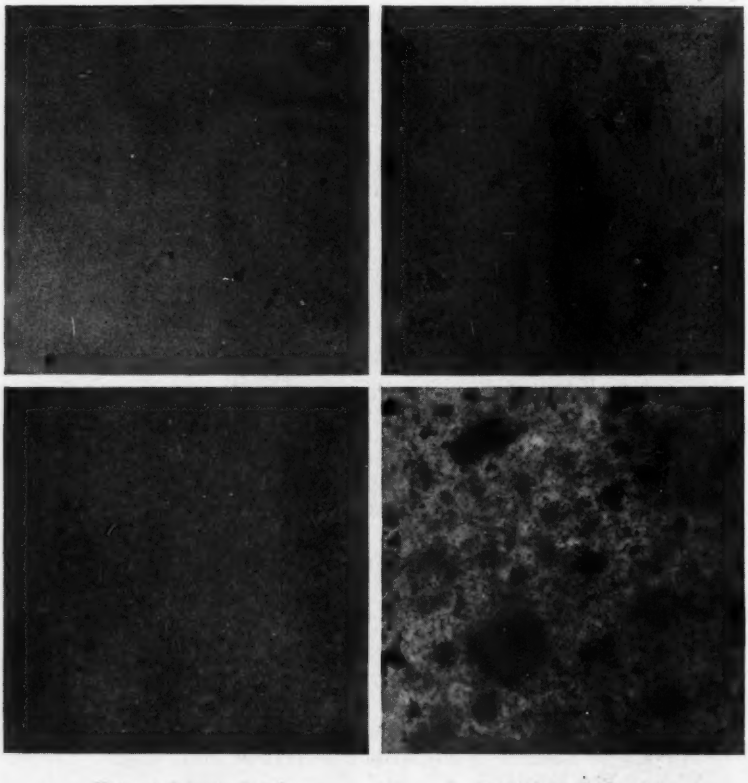


FIGURE 4. APPEARANCE OF SQUEEZE-OUT SECTIONS OF FINAL STOCKS

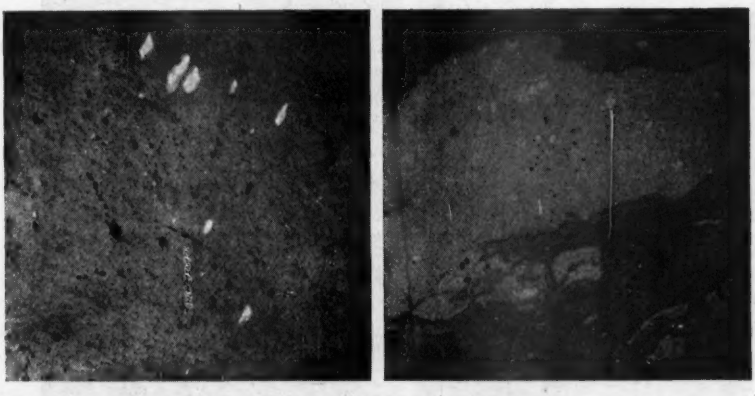
Effect of Further Milling and Mixing with Additional Rubber

Park and Morris (*11*) showed that batches set up by mill "scorching" have a granular structure when examined by the method of Roninger (*12*) and that this structure is exceedingly persistent when the mix is subjected to further mastication and mechanical working. In order to determine more

accurately the behavior of abnormally stiffened rubber–carbon black batches when further milled, a batch of the following composition was mixed:

	Composition, Vol.	As Mixed, Grams
Smoked sheet rubber	100	2500
Rubber channel black	67	1665

The batch was milled for 20 minutes on a 16-inch (41-cm.) laboratory mill, allowing 3 minutes for breaking down the rubber, 7 minutes for adding the pigment, and 10 minutes for mixing. A section of the stock prepared by the Roninger method is shown in Figure 3. The appearance of the section is normal for such a mix. The batch was then split into two



Unheated master batch Heated master batch

FIGURE 5. POLISHED SECTIONS OF FINAL STOCKS (× 100)

The flakes of lighter colored material in the stock made from heated master batch are evidently undispersed master batch which grade down in size to particles below the limit of resolution. These particles appear to be made up of the material shown in the treated master batch of Figure 4.

portions, and one portion was treated in a manner similar to that used by Busse and Davies, nitrogen being used in the heating chamber to avoid excessive oxidation. The time and temperature of treatment was 8 hours at 132° C.

The treated and untreated portions were then milled by identical procedures into final batches having the following formulas:

		As Mixed	
	Composition	Heated	Unheated
Smoked sheet rubber	100	400	400
Unheated master batch	...	...	167
Heated master batch	...	167	...
ZnO	5	25	25
Sulfur	2.2	11	11
Mercaptobenzothiazole	1.25	6.25	6.25
Rubber channel black	13.4	...	...

Microsections of these batches made by the method of Allen are shown in Figure 4. It is apparent that the heated master

batch was merely torn apart and distributed in the final mix, mainly in the form of discrete lumps, whereas the untreated batch blended uniformly with the rest of the rubber.

The fact that the undispersed lumps shown in the two right-hand photomicrographs of Figure 4 are master batch is much more clearly demonstrated in Figure 5 where the lighter colored patches in the Roninger sections of the stock made

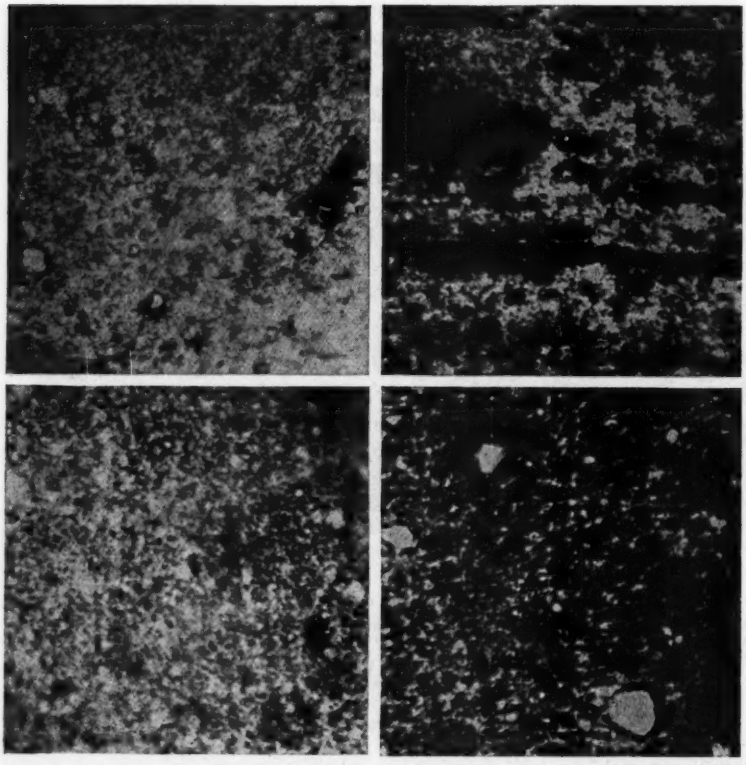


FIGURE 6. MICROTOME SECTIONS SHOWING THE EFFECT OF REMILLING STOCKS MADE FROM HEATED AND UNHEATED MASTER BATCH (× 1350)

from treated rubber may be recognized as master batch by comparison with Figure 3.

Perhaps the clearest demonstration of the roughness and inhomogeneity of the final stock made from heated master batch is shown in the microtome sections of Figure 6. Rubber is a rather difficult subject to slice successfully, but these sections show not only that the final batch as originally milled was highly discontinuous but that passing the rubber

twice through a cold 12-inch (30-cm.) mill with the rolls set as close as possible on the second pass resulted only in a decrease in the size of the aggregates or lumps, the space between remaining clear.

Discussion

While this work showed definitely that carbon black flocculates in rubber as in paint mixtures (Figure 7) and that stiffness accompanies the phenomenon, a cause and effect relation has not been clearly established. Presumably the flocculation of the pigment contributes in some meas-

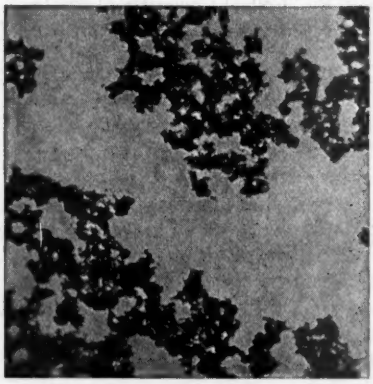


FIGURE 7. CHANNEL CARBON BLACK FLOCCULATED IN LINSEED OIL

ure to the so-called reinforcing effect; but in view of the findings of Menadue (*10*), who found the rubber stiffer than it was originally when almost all the pigment had been removed (by acid extraction in the case of magnesium carbonate and zinc oxide), it is necessary to reserve judgment until further data are at hand.

If stiffening of pigment-rubber master batches at milling and vulcanizing temperatures is due in any measure to flocculation, it is highly probable that this structural rearrangement also takes place to some extent in ordinary milled tread stocks during the early portion of the vulcanization process. The data here given furnish reasonably substantial evidence for the views of Depew and Ruby and of Green regarding the relation of flocculation to the reinforcing effect of carbon black in vulcanized rubber.

Acknowledgment

The writers wish to thank the Firestone Tire & Rubber Company for kind permission to publish this work.

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Processing Characteristics of Rubber Compounds - - -

Effect of Pigment Particle Size and Surface

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A STUDY of the processing properties imparted by any pigment to a rubber compound is important in determining the most effective and economical type of pigment for a particular purpose. For example, in a truck tire carcass compound where zinc oxide may be the main pigment, in order to obtain the maximum quality this zinc oxide should be of the type which will give a soft uncured stock and free-flowing qualities so that the cords in the carcass may be thoroughly impregnated during the calendering and curing processes. Also, in a tread compound where channel black is the main pigment, that type of black which will allow faster incorporation into the rubber, faster extrusion, and better flowing qualities will result in manufacturing economies. In the case of both the zinc oxides and the carbon blacks it is essential that these desirable processing characteristics be obtained without losses in other properties, such as rate of cure, tensile strength, and abrasion resistance.

Table I. Measurements for Zinc Oxide–Smoked Sheet Master Batches

Zinc Oxide	G_z	M	G_z/M	Relative Fineness	Relative Tubing Speed
A	51.45	2.15	23.9	1	8
B	65.64	1.17	33.2	3	5
C	83.15	1.14	73.0	5	4
D	99.93	0.71	140.7	8	1
E	57.38	2.65	21.6	2	7
F	64.24	2.63	24.4	4	6
G	87.56	0.75	116.8	6	3
H	88.67	0.73	121.5	7	2

Nellen (*3*) recently described a tubing machine plastometer for the determination of the working qualities of rubber; Gamble and Barnett (*1*) discussed a method of measuring the relative particle size and size distribution of pigments, based on their scattering characteristics in the visible and near infrared portions of the spectrum. The work discussed in this report was undertaken to determine, by application of

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the methods described in these papers (*1*, *3*), the relative importance of the particle size of pigments and the nature of the surface, in controlling the factory processing of pigments in rubber.

Tubing Machine

In the operation of the tubing machine, the rubber is cut into small pieces and fed into the hopper; after exactly 200 grams have been run through to bring the rubber in the machine and the die to a constant temperature, three 1-minute samples are cut off by means of a cutter fastened in front of the die. During the extrusion of these samples, the temperature of the extruding rubber, power readings, and circulating water temperatures are noted. The three samples are weighed individually and their average recorded as grams extruded per minute (G_s in the tables). The loaded machine is held for 3 minutes; then by means of pressure applied to the diaphragm, the die is forced back against the rubber in the machine and the time required to extrude 5.4 cc. of compound is recorded as M. The factor G_s is a direct measure of the tubing speed, M is an inverse measure of plastic flow, and the relation G_s/M combines the two as a measure of the plasticity of the stock. Further details of the machine and its operation are given in the original article (*3*).

Particle Size of Pigments

The particle size examination is carried out on the same compounds that are prepared for the measurement of the rubber properties. These compounds are made into suspensions of known constant concentration with carbon tetrachloride, and the percentage of light transmitted by the pigmented suspension is measured from the visible blue to a wave length of about 4.0 microns in the infrared in comparison with an equivalent suspension of unpigmented rubber. The size and size distribution characteristics of the pigment are related to the shape of this curve by the following considerations: Low transmission in the short wave-length region is indicative of small particle size, and the greater the selectivity (slope of the transmission curve towards longer wave lengths) accompanying the low transmission, the finer is the particle size. High transmission in the short wave-length region without selectivity is indicative of coarse particle size. Low transmission in the long wave-length region is also indicative of a large particle size. The average particle size of the pigment is roughly indicated by the point in the spectral transmission curve at which selectivity begins to develop. This occurs at a point where the particle size approaches the magnitude of the wave length. A more detailed account of the method is given in the original article (*1*).

Table I shows the measurements obtained on the tubing machine for a series of 61–39 zinc oxide–smoked sheet master

batches. The master batches were prepared on a laboratory mill, using a milling procedure which had been checked for reproducibility in the plasticity test. In three checks on the milling procedure, values for G_s were obtained of 16.64, 16.75, and 16.74. Zinc oxides A, B, C, and D are of the fast-curing variety and were prepared to cover a wide range of size characteristics; E, F, G, and H represent a similar series in the slow-curing type. From the method of manufacture it would be expected that the first four zinc oxides would have similar surface characteristics and also the last four, but that there might be considerable difference between the two series. The particle size characteristics of these zinc oxide samples are shown by the transmission curves of Figure 1. Pigments A, B, and E give curves of low transmission in the short wave-

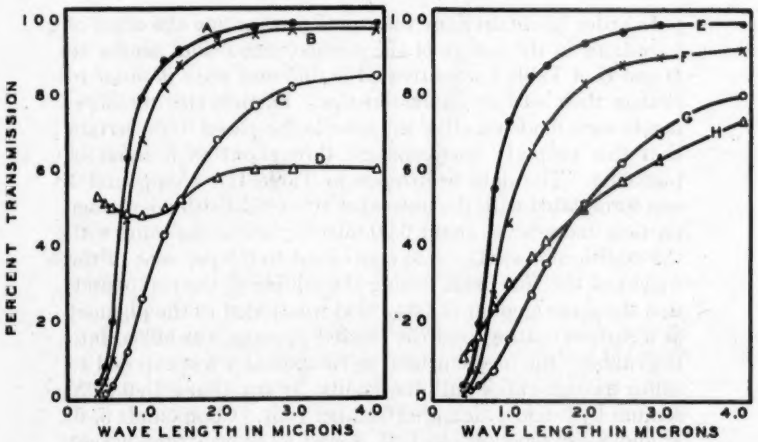

FIGURE 1. INFRARED TRANSMISSION CURVES OF ZINC OXIDES

length region, and high selectivity and high transmission in the longer wave lengths; all properties indicate fine particle size and a high degree of uniformity of particle size distribution. From the position of the selective portion of these curves with reference to the wave-length scale, A is shown to be finer than either B or E, and E very slightly finer than B. Sample D is by far the coarsest oxide in the series, as indicated by high transmission in the short wave-length region, relatively low transmission at the long wave lengths, and an almost complete lack of selectivity. Zinc oxides F, C, G, and H fall in between these extremes and in that order of increasing particle size and decreasing uniformity of particle size distribution. From the previous discussion it is seen how this conclusion follows from the transmission curves. The data in Table I show that within each series the tubing speed increases, while M decreases and G_s/M increases with increasing particle size of the zinc oxide. The relative order of

the oxides with respect to particle size and tubing speed is also given in Table I, and the agreement between the two properties is very good, even when both the slow- and fast-curing types are included in the comparison. The plasticity of the entire series of samples does not show as good correlation with the size characteristics as does the tubing speed, yet all of the discrepancies occur with the four pigments of finest particle size. For example, although sample B is considerably finer than F, it produces a softer and more plastic stock. These data show clearly that the working properties of a pigmented rubber compound vary directly with the particle size characteristics if the condition of the surface is the same.

Nature of the Surface

In order to obtain more information regarding the effect of variations in the nature of the surface, zinc oxides similar to B and C of Table I were treated in different ways in order to change their surface characteristics. Particle size measurements were made on all of the samples prepared to be certain that this property was constant throughout each series of pigments. The data are shown in Table II. Compound 1 was formulated with the untreated zinc oxide with an average particle diameter of about 0.20 micron; 2 was the same with the addition of a fatty acid equivalent to 0.3 per cent of the weight of the zinc oxide during the milling of the compound; in 3 the same amount of fatty acid was added to the pigment as a surface coating, and the treated pigment was milled into the rubber; the pigment used in compound 4 was exposed to sulfur trioxide vapor until the acidity, by titration with 0.01 *N* sodium hydroxide, measured 0.23 per cent. Compounds 5, 6, 7, and 8 corresponded to 1, 2, 3, and 4, respectively, except

Table II. Effect of Variations in the Nature of the Surface

Compound	G_z	M	G_zM	Compound	G_z	M	G_zM
1	59.08	1.54	38.4	5	83.71	0.95	88.2
2	64.57	1.35	47.9	6	96.56	0.66	146.5
3	82.36	0.71	116.0	7	99.56	0.53	188.5
4	52.23	2.19	23.8	8	83.47	0.96	86.9

that the base pigment had an average diameter of about 0.40 micron. The pigment-rubber ratio was the same as in the compounds of Table I. The data in Table II show that the changes made in the character of the surface of the finer zinc oxide produce nearly as much variation in the working properties as did the extreme variations in particle size shown in Table I. In the case of the coarser zinc oxide the differences in tubing rate caused by alteration of the surface of the pigment were slight, although the plasticity was increased con-

siderably in the case of the pigment which had been surface-coated with fatty acid. This result undoubtedly explains the behavior of the pigments in Table I. Surface effects seem to be of great importance in the case of the finer pigments; when the particles are above a certain diameter, good working properties are obtained regardless of the nature of their surface. The sulfur trioxide treatment of the finer pigment decreases the tubing rate and the plasticity in comparison with the untreated pigment; in the case of the coarser zinc oxide this exposure to sulfur trioxide was without effect on the working properties. The use of a pigment which had been surface-coated with fatty acid prior to incorporation had a much greater effect on the working properties than the addition of the same amount of fatty acid to the compound during milling. Surface treatment of the finer pigment with fatty acid resulted in a marked increase in the tubing rate and softness of the master batch. With the coarser oxide the resulting increase in the tubing rate of the rubber batch was slight but the increase in plasticity was obtained.

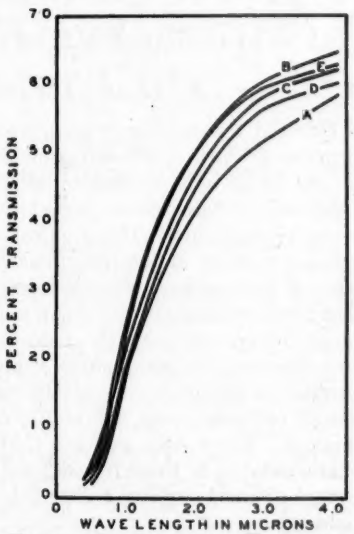

FIGURE 2. INFRARED TRANSMISSION CURVES OF CHANNEL BLACKS

In the course of this investigation, experiments were made with samples of carbon black, precipitated whiting, ground limestone rock, and clay; while it was not possible to control the size and surface properties as was done with the zinc oxides, the general conclusions are the same. The processing properties improve as the particle size of the pigment increases if the surfaces are similar; if the pigments are coarse enough, the nature of the surface will be of minor importance in determining the processing quality but the finer materials such as certain precipitated whitings are highly sensitive to changes in the surface. In this connection, some results obtained with channel-process carbon blacks may be of interest.

Five different carbon blacks were selected, representing a wide range of working properties of this pigment. The samples were milled into the rubber with 55 parts of pigment to 100 parts of rubber and 4 per cent of softener; check batches were prepared with each pigment. The following results are

the average values obtained for each pigment on the tubing machine and demonstrate that considerable variation exists in the working properties of these carbon blacks:

Carbon Black	G_x	Carbon Black	G_x
514	10.41	711	23.71
522	16.71	774	20.08
		775	18.00

Infrared transmission curves were also measured for suspensions of each of the compounds and are shown in Figure 2. So far as it is possible to determine by this method, no significant differences in particle size are indicated in this series of pigments. The application of the infrared transmission method in the determination of the size characteristics of carbon blacks was discussed in the previous paper (*1*). The average diameter of carbon blacks 514 and 775 was also measured by counting the number of particles in a Nujol suspension of the compounds, using the ultramicroscope according to the procedure of Gehman and Morris (*2*). The values obtained were within the experimental error of the method. These data indicate that the difference in tubing characteristics of these blacks results from differences in the nature of their surfaces rather than from differences in particle size.

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Extraction of Water-Soluble Accelerators in Water Cure

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LATEX products are usually vulcanized at relatively low temperatures, below 212° F. (100° C.), because ultra-accelerators can be used without the danger of scorching. These low-temperature cures may be carried out in air or in water. The use of water-soluble accelerators in water cures has been subject to considerable controversy inasmuch as it is believed that they are extracted in this type of cure. This paper is presented to show that the common and well-known water-soluble accelerators are not extracted from the rubber film during vulcanization in water.

Since ultra-accelerators are very scorchy (*3*), they were used in "split batches"; i. e., the sulfur and accelerator were mixed in separate stocks on the rubber mill. Vulcanization was effected either by mixing the two stocks on a mill immediately before use or by superimposing thin layers of these stocks upon each other. In the latter method the vulcanization was entirely dependent upon the migration of sulfur and accelerator from one layer into the other. The split-batch rubber compound developed into the water cure where a rubber film containing sulfur, zinc oxide, etc., and no accelerator or a very slow accelerator was immersed in a hot water solution or dispersion of an ultra-accelerator. The water functioned as a carrier for the accelerator and as a medium supplying the heat necessary for rapid vulcanization. The accelerators used in this process were carbon disulfide reaction products of dimethylamine, piperidine, etc., and xanthates or their sodium or potassium salts, as well as tetramethylthiuram monosulfide, which are water soluble; water-insoluble accelerators were employed, such as the carbon disulfide reaction products of methylenedipiperidine, etc., or the metallic salts of dithiocarbamates, some of which are liquid and others solid at the water temperatures used.

The vulcanization of latex products may be carried out by either of the methods outlined. Since no milling is necessary, scorching is eliminated and the complete formula containing sulfur, zinc oxide, ultra-accelerator, etc., is prepared. Since latex is an aqueous dispersion of rubber, the use of water-soluble vulcanizing ingredients seems desirable because they remain in solution whereas insolubles tend to settle out from

low-viscosity mixes. Consequently, the tolerances in the quantity of accelerator required to obtain a desired cure are very narrow.

It is an accepted fact that an accelerator will migrate or dissolve into a rubber film which is immersed into an aqueous solution or dispersion of accelerator and will thus effect vulcanization. However, it is possible that a vulcanizable film of rubber containing a water-soluble accelerator will have this accelerator partially extracted during water cure (*5*) and thus result in wide variations in the properties of the finished product. The water in this case is used only as a medium to supply the heat required for rapid vulcanization. The term "rubber film" is used because a latex compound on

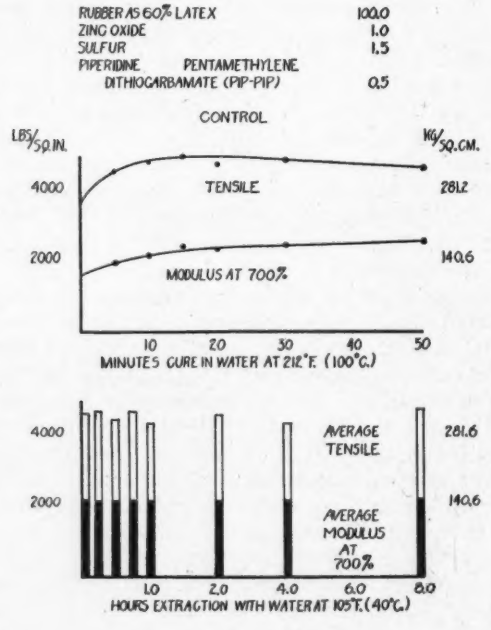

FIGURE 1

the removal of substantially all of its water content is a rubber film, and the vulcanization of latex as latex is vulcanization in aqueous solution.

Extraction of Compounds

The latex compounds given below were mixed and films were poured as described in a previous article (*4*):

These 10 × 14 inch (25.4 × 35.6 cm.) rubber films were allowed to dry 8 hours under controlled humidity free from drafts until

set, when the chamber was opened and air was circulated over their surface with an electric fan to accelerate drying. At the end of this period the rubber films were sufficiently dry to handle but were still opaque and suitable for extraction.

A 20-liter container was fitted with a water inlet near the bottom and an overflow at approximately 18 liters capacity with water changing at approximately 20 liters per hour. This container was heated on a hot plate, and the temperature maintained at 105° F. ± 2° (40° C.); this was the highest temperature that would not produce appreciable vulcanization in 8 hours in any compound employed.

The 10 × 14 inch rubber films, each weighing approximately 125 grams, were extracted 0.25, 0.50, 0.75, 1.0, 2.0, 4.0, and 8.0 hours except as noted in Figure 4. The rubber film for the 8-hour extraction was removed from the glass plate, marked with a metal tag, and submerged by weights attached to one end in the 20-liter container. The film for the control stock was also placed in the container for 1 minute and then removed, and the 0.25-hour extraction was carried out. In this way only two rubber films were subjected to extraction at one time. The container was agitated with a paddle at least every 15 minutes to ensure thorough circulation. The rubber films, on removal from the extraction process, were placed on clean glass sheets in a cabinet at 70° F. (21° C.) and 80 to 90 per cent humidity to prevent their drying. On completion of the 8-hour extraction, all of the rubber films were suspended from a line to dry for 20 hours at 70° F. before being cured.

These dry rubber films were cut into six pieces measuring 3.25 × 5.5 inches (8.25 × 13.9 cm.) each; a 3 × 14 inch (7.6 × 35.6 cm.) strip across the end was held for a check on prevulcanization or cure during the drying period. Vulcanization or curing was carried out in water at 212° F. over a range of cures suitable for the respective acceleration. Water curing was preferred because the temperature is uniform and there is no lag as in dry-air cures. Each of the six 3.25 × 5.5 inch pieces had a hole punched in one end by means of which it was threaded on a glass rod. The rod kept the pieces submerged and made their individual removal convenient. Each set of six pieces from one period of extraction was cured in a 1500-cc. beaker containing approximately 1200 cc. of distilled water. The individual pieces were removed on completion of the desired cure and placed on clean glass sheets until the last piece had been cured. They were then all suspended from a line to dry overnight at 70° F. before the preparation of dumbbell test pieces.

Three dumbbell test pieces were cut from each strip by means of a standard A. S. T. M. die and suspended on wires (twenty-one on each wire) for approximately 44 hours in a conditioning cabinet at zero per cent humidity and 70° F. before being tested. Twenty-one test pieces (one extraction) were removed from the conditioning cabinet at one time and broken on the Scott tester (4). All the test pieces of one compound were broken by the same operator within 6 hours. The results as presented are the average results of the best two or, generally, all three test pieces from a given cure.

In order to simplify the presentation of the test data, the curves for tensile strength and modulus at 700 per cent elongation of the control stock, which is representative of the series, are given. The effect of extraction is shown graphically by taking the average results of tensile strength and modulus at 700 per cent elongation for all seven cures for each period of extraction.

The approximate solubilities of accelerators tested are as follows:

	Parts Sol. in 100 Parts Solvent at 105° F.	
	Water	0.10% NaOH
Piperidine pentamethylenedithiocarbamate	8	100
Sodium or potassium pentamethylenedithiocarbamate (*2*)	100	100
Sodium or potassium mercaptobenzothiazole (*1*)	100	100
Zinc dibutyldithiocarbamate (*5*)	None	None

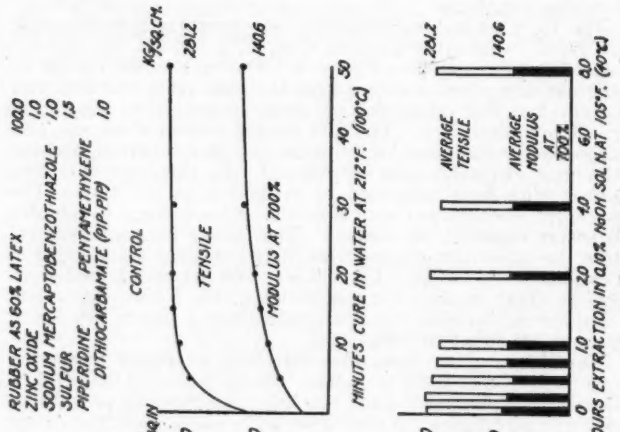

FIGURE 3

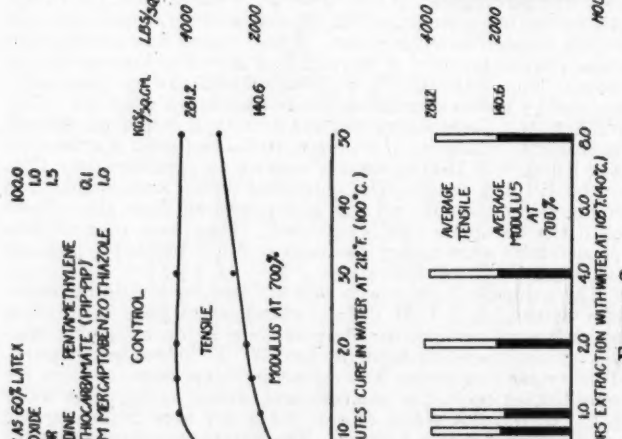

FIGURE 2

Piperidine Pentamethylene-dithiocarbamate

A typical and well-known latex formula is shown in Figure 1. Physical tests were made on 5-, 10-, 15-, 20-, 30-, and 50-

minute cures in water at 212° F. The tensile and modulus curves at 700 per cent elongation are shown in the upper part of Figure 1, and the lower part shows the effect of the extraction with water on this compound. The differences in average physical properties are negligible or well within the experimental error. The eight rubber films extracted had an

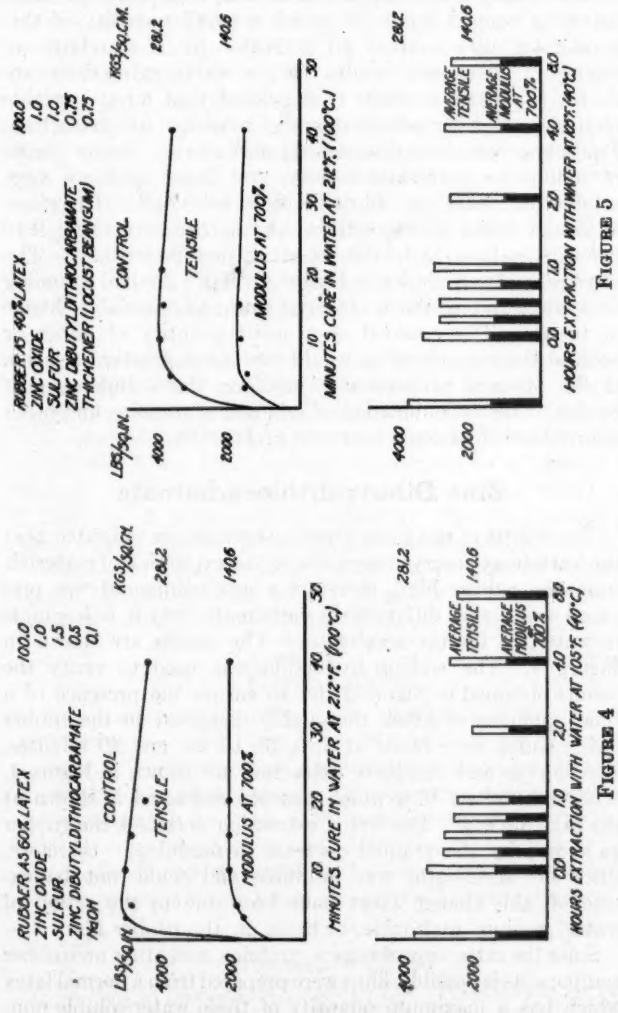

FIGURE 4

FIGURE 5

approximate total weight of 1000 grams and would contain approximately 5 grams of accelerator. Over a period of 8 hours approximately 5 grams of accelerator were subjected to extraction in 160,000 grams of water (20 liters per hour for 8 hours), which is approximately three thousand times the quantity of water required to dissolve this accelerator.

Therefore the accelerator (piperidine pentamethylenedithiocarbamate) must have a selective solubility for rubber since there is no appreciable difference between the control and the 8-hour extraction.

The possibility that as little as 0.05 per cent of the piperidine pentamethylenedithiocarbamate, based on the rubber content, was extracted in the first series of tests led to a second series, in which a small quantity of this accelerator was used as an activator for a standard accelerator. The test results of the water extractions are shown in Figure 2 where it is evident that no appreciable quantity of either accelerator was removed by extraction. Piperidine pentamethylenedithiocarbamate forms salts of sodium or potassium readily, and these salts are very soluble in water or dilute caustic solutions. Therefore, a second series of extractions was carried out using 0.10 per cent sodium hydroxide as an extraction medium. The physical tests are shown in Figure 3 where a gradual softening or decrease in modulus is observed with no appreciable change in tensile. The removal of a small quantity of either or both of these accelerators would produce a greater variation in the physical properties. Therefore, this softening must be due to the saponification or removal of proteins and other nonrubber components from the rubber film.

Zinc Dibutyldithiocarbamate

The results of the three previous extractions indicated that the variations observed were due to the extraction of materials from the rubber film; therefore a new compound was prepared using zinc dibutyldithiocarbamate (which is insoluble in water, *5*) for the accelerator. The results are shown in Figure 4. The sodium hydroxide was used to verify the results obtained in Figure 3 and to ensure the presence of a small quantity of alkali thoroughly dispersed in the rubber film. Cures were made at 3, 5, 10, 15, 20, and 40 minutes. The curves and results of extraction are shown in Figure 4. A second control film which was not extracted is shown at the extreme left. The water extraction softened the rubber as shown by the gradual decrease in modulus; therefore, since the accelerator was insoluble and could not be extracted, this change must have been due to the action of water, sodium hydroxide, or both, on the rubber film.

Since the extraction of sugars, proteins, and other nonrubber components is possible, films were prepared from a normal latex which has a maximum quantity of these water-soluble nonrubber components. Zinc dibutyldithiocarbamate accelerator was used, and the accelerator and sulfur ratios were adjusted to approximate the cure in Figure 4. The results of the physical tests on these extractions are shown in Figure 5 where a marked softening is evident during the first hour of extraction. Since the accelerator was insoluble, this

softening was due to the removal of nonrubber components from the rubber film by the water extraction.

Effect of Extraction

In the five series of extractions discussed, a gradual loss of rigidity was observed in the dry rubber film with increasing time of extraction before and after cure. In tests comparing ordinary centrifuged latex with latex centrifuged and diluted two, three, or four times, a similar softening was observed. In a study of the effect of humidity on the physical tests of latex rubber compounds (*4*) it was evident that the water cures adsorbed less moisture than the air cures of the same compound; this behavior indicated that the water removed solubles from the rubber film. This extraction or leaching out of water-soluble nonrubber components is well known and is general practice with the manufacturers of latex products. It is carried out before or after cure with equal success, and gives a softer and less water-adsorbent article.

The tests discussed were carried out on semidry, uncured latex rubber films, and it is believed that bone-dry or even cured films will produce similar results. However, under no conditions should tests be attempted on latex rubber films which are so wet that they will disintegrate on immersion in water. In practice, latex products are trimmed and may have a bead rolled before vulcanization; in order to accomplish these operations, the film must be comparatively dry. The immersion of a too wet latex rubber film in water for vulcanization causes distortion which vulcanizes in this unnatural condition and is too evident in the finished product.

Conclusions

No measurable quantity of the water-soluble accelerators tested was extracted from the rubber during the water extraction. Therefore, these accelerators will not be extracted during vulcanization in water. The softening action observed in water-cured latex products is due to the extraction of water-soluble nonrubber components from the rubber film. The water-soluble accelerators tested have a selective solubility for rubber which is many times greater than their solubility in water.

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Control Tests of Uniformity in the Manufacture of Carbon Black

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Twenty-five years ago, a pneumatic tire for an automobile cost twenty-five dollars and gave service of about 3500 miles. Today a pneumatic tire costs only one-half as much and can be relied upon to give service of about 25,000 miles. These improvements are the result of various factors, such as the use of cord fabric, organic accelerators, antioxidants, and other carefully chosen raw materials. Among these latter, it is safe to say that carbon black is unquestionably the raw material which has contributed most of all to the increased mileage of pneumatic tires.

Years ago when the reënforcing properties imparted to rubber by carbon black first became recognized, this product was furnished without any particular requirements other than freedom from impurities. Later, as the percentage of carbon black incorporated in rubber mixtures continued to increase, certain measures were taken to control the grit content. Ultimately, with the aim of furnishing the rubber industry with a product of the highest quality and greatest uniformity, the most important producers of carbon black, in coöperation with the laboratories of rubber factories, proceeded to develop a series of check tests and various other tests, which have led in turn to the development of the present-day specifications of carbon black.

With improvements in methods of manufacturing carbon black, grit has been practically eliminated, and today only traces are found, and these but rarely.

In carbon black factories, daily tests are now made for grit, moisture, ash, volatile matter, adsorption of accelerators, and p_H value.

To maintain control of the uniformity of size of the carbon black particles, resort is had to a turbidity test carried out in aqueous medium. Sedimentation is allowed to continue in a graduated cylinder of 200 cc. capacity for a definite period of time, and the rate of sedimentation is measured automatically by a photoelectric cell. When compared with standard tables, the values obtained give a fairly precise indication of the particle size distribution in the sample.

Tests of the dispersion of carbon black in a rubber mixture prepared in a Schiller or Banbury mixer are also carried out. The degree of dispersion is judged by examining torn surfaces under the microscope, as described by Allen and Schoenfeld (cf. *Ind. Eng. Chem.*, **25**, 994, 1102 (1933)), or microtome sections under high magnification as described by Allen (cf. *Ind. Eng. Chem., Anal. Ed.*, **2**, 311 (1930); Rubber Chem. and Tech., **3**, 755 (1930)).

To ascertain the ease of processing of an unvulcanized mixture containing any particular quantity of carbon black on a mixing mill, its plasticity is determined by the Williams method. Other tests include determinations of tensile strength, modulus, elongation at rupture, and resistance to abrasion, as well as aging tests in a Geer oven at 70° C. for 7 to 14 days or in an oxygen bomb at 82° C. under 300 lb. per sq. pressure for 24 hrs.

To measure the resilience of a rubber mixture containing carbon black, the mixture is tested on a pendulum machine, which gives an indication of the tendency of a tire tread to crack when flexed and to resist wear and abrasion. In so far as abrasion tests are concerned, the personal experience of the author is that no laboratory apparatus indicates with any degree of certainty the resistance of a pneumatic tire to road wear. As a matter of fact, even when two tire tread mixtures give apparently satisfactory laboratory tests, it is difficult to guarantee that, on passing from laboratory to road tests, these laboratory results on resistance to abrasion will be confirmed on the road.

Finally, hardness tests are made with a Shore instrument, or with a Tinius Olsen durometer, the aim of which is to check the state of cure or the volume of carbon black in a mixture. The so-called T-50 test of Gibbons, Gerke, and Tingey (cf. *Ind. Eng. Chem., Anal. Ed.*, **5**, 279 (1933); RUBBER CHEM. AND TECH., **6**, 525 (1933)) is a simple and sensitive method for determining the state of vulcanization.

In brief, eighteen distinct tests are carried out daily in the laboratories of the principal manufacturers of carbon black with a view to controlling the uniformity in quality of the carbon black produced. These tests give an accurate picture of carbon black in so far as its physical state is concerned, both with respect to its incorporation into unvulcanized rubber mixtures and its effects on the vulcanized product.

Since the need of foreseeing the properties imparted to unvulcanized rubber by carbon black became generally recognized, it has come to be realized that the Williams plastometer does not give either a sensitive or a generally satisfactory indication of these effects. Consequently tests have been carried out in a laboratory extruding machine with mixtures composed of:

Rubber	100
Carbon black	55
Stearic acid	4

These mixtures were prepared in the laboratory under standardized conditions, were then extruded through a die $^1/_8$ inch in diameter, and the weights of the mixtures extruded per minute and the times necessary to extrude 5.5 cc. were measured.

By dividing the first result by the second result, a factor is obtained which gives a good indication of the ease of processing of the carbon black. Experience has shown that when this factor lies between 4.5 and 7.0, the mixture has excellent processing qualities.

To illustrate the sensitivity of this test, as well as its superiority over the ordinary plastometer, the following experimental results are offered:

Mixture	Modulus (Lb. per Sq. In. at 300% Elongation)	Tensile Strength (Lb. per Sq. In.)	Elongation at Rupture (Percentage)	Plasticity (Williams)	Extrusion Index
A	1550	4500	540	100.0	6.00
B	1560	4460	530	100.5	2.09
C	1590	4450	550	100.6	5.80
D	1570	4490	540	101.4	3.20

It is evident from these results that, disregarding the extrusion indices in the last columns, mixtures A, B, C, and D must be regarded as essentially the same. Nevertheless the extrusion indices indicate clearly that mixture B and mixture D would behave badly during processing, and this was verified in factory operation. Whereas mixture A extruded extremely well, mixture B extruded so badly that it was impossible to form a tread. Mixture C behaved very well, whereas mixture D was extremely difficult to extrude.

In view of these facts, all the principal manufacturers of carbon black now maintain strict control of the processing quality of their blacks. This represents one more step forward in the improvement and maintenance of uniformity of quality of the carbon black furnished to the rubber industry.